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Multimedia Assessment of Pollution Potentials of Non-Sulfur Chemical Pulping Technology

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FOREWORD

When energy and material resources are extracted, processed, converted, and used, the related pollutional impacts on our environment and even on our health often require that new and increasingly more efficient pollution control methods be used. The Industrial Environmental Research Laboratory-Cincinnati (IERL-Ci) assists in developing and demonstrating new and improved methodologies that will meet these needs both efficiently and economically.

A severe odor problem is caused by reduced sulfur compounds in the kraft process. The pulping industry has been developing new pulping technology to replace the kraft process with processes that do not contain sulfur and thus eliminate the odor problem. This report assesses the potential air, water, and solid waste pollution and energy use of new and non-sulfur pulping technologies. A forward look to the potential pollution reductions or hazards and energy use of these evolving pulping technologies will help the agency make decisions on supporting research on specific technologies. Investigations can be implemented on problem areas before the processes are implemented.

All of the proposed new pulping processes reduce odor emissions, but generally at the expense of greater SO_2 and particulate emissions. Expected BOD, suspended solids, color, and toxicity are generally lower than expected from a kraft mill. Some of the new processes will require less energy and others will require more energy than does the kraft process.

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Director
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ABSTRACT

This report gives an estimate of the air, water, and solid waste pollution generated by developing and existing non-sulfur pulping techniques that are potentially competitive with kraft pulping. Also developed were energy use and needs estimates for these pulping processes. Processes investigated were soda pulping, soda semichemical pulping, soda pulping followed by oxygen delignification, thermomechanical pulping followed by oxygen delignification, oxygen pulping of wood wafers, chlorine dioxide pulping, solvent pulping and the Rapson process.

All of the pulping processes considered develop less water pollutants and less total reduced sulfur emissions than does the kraft process. Sulfur dioxide and particulate emissions vary from process to process, some being greater than that expected from kraft and some less. Sulfur dioxide and particulate emissions largely originate from power boilers. Requirements for power produced from power boilers vary considerably between mill types. Some air pollutants presently not inherent to the production of pulp, such as sodium iodide, hydrochloric acid, and carbon monoxide, are potentially emitted from several of the new pulping processes.

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SECTION 1

INTRODUCTION

Environmental pressures have caused the pulp and paper industry to develop new pulping processes and significantly modify existing processes. The changes proposed are often a result of specific pollution problems such as color, BOD, or odor emissions. The reduction of one specific pollutant may cause an increase in other pollutants. This paper evaluates the air, water, and solid waste pollutants from some of the more promising new pulping technologies, as well as from some existing technologies that may gain in popularity.

The goals of the processes being developed are generally aimed toward the reduction of reduced sulfur compounds (odors), reduction of color from the bleach plant, or elimination reduced sulfur emissions. Non-sulfur processes include soda pulping, oxygen pulping, halogen pulping, thermomechanical pulping, solvent pulping, and nitric acid pulping. Reuse of bleach plant effluents and eventual disposal into the kraft recovery system is aimed at elimination of colored effluents or the elimination of all effluents. These processes include the Rapson process and electrostatic precipitator dust catch leaching.

Pollutants investigated in this report are: 1) air-reduced sulfur compounds (odors), sulfur dioxide, particulates, and chlorides; 2) water-BOD, suspended solids, color, and toxicity; 3) and solid wastes. Some processes generate nontypical pollutants particular to that process. These will be discussed individually in the sections covering the particular process. Energy requirements for the new processes are also discussed.

PROCESSES INVESTIGATED

Two soda pulping processes are discussed herein: full soda pulping, and soda semichemical pulping. Although they are similar processes there are enough differences between the two to result in different pollutional characteristics. Although soda pulping is an old and well known process, it is included because of its low-odor potential.

Several process configurations have been developed for oxygen pulping. These processes include oxygen pulping of thin chips, soda pulping followed by oxygen delignification, and thermochemical pulping followed by oxygen delignification. An alkaline sulfite pulping-oxygen delignification process and oxygen alkali semichemical process have also been proposed. The first 3 aforementioned processes will be examined separately since each has its distinctive pollution characteristics. The latter two are not examined in this paper.

Halogen pulping is of interest to the pulp and paper industry because of the high strength pulps produced at high yields. Although there are problems to be solved, such as optimum process configuration and the high cost of pulping chemicals, this process offers many potential advantages over the kraft process.

An occasional journal article appears on solvent pulping indicating that the process is still being considered for commercial development. The processes are being designed with lignin by-product production in mind and with air pollution control as a major side benefit.

Although the Rapson process is not a sulfur-free process it is included because of some potential air pollution problems, it is a new development, and because it does not produce a contaminated water discharge.

PROCESSES NOT INVESTIGATED

Nitric acid pulping is not included because of a lack of industry interest due to high pulping chemical cost, corrosion, and cooking liquor disposal problems. Emission of toxic nitrogen oxides is also a potential problem (1).

SECTION 2

CONCLUSIONS

Each of the pulping processes studied in this paper has its own potential pollution problems, but they are generally less than would come from a kraft mill. Some of the new pulping processes are designed to reduce air pollution and some to reduce water pollution. The result is generally a decrease in most pollution parameters but an increase in a few other pollution parameters, or in some cases, the creation of a new pollutant not indigenous to the present pulping industry. The increased pollutants resulted from power production in boilers due to the higher energy requirements of some of the new pulping processes compared to kraft. All of the new processes result in the reduction of odors due to reduced sulfur, less BOD, less suspended solids, less color, and lower toxicity. The process that shows the lowest air and water pollution problems is production of pulp by high pressure thermomechanical defiberation followed by oxygen delignification. Table 1 lists the estimated pollution parameters for the processes investigated.

The values presented in Table 1 are estimates. Improvements in the probable process configurations assumed may alter the results presented. For instance, pulping at higher consistencies in any of the oxygen pulping processes will reduce evaporation energy requirements and hence may reduce total energy requirements and, therefore, SO_2 and particulate emissions.

TABLE 1. SUMMARY OF RESULTS
All values are given as kg/metric ton pulp (lb/ton) except energy

Parameter	Kraft	Soda	Semi Chem.	Oxygen Soda	Therm. Mech.	Oxygen Chips	Chlorine Dioxide	Solvent	Rapson
Air									
Reduced Sulfur	0.12 (0.25)	0.0002 (0.0004)	0.0002 (0.0004)	.0002 (.0004)	0 (0)	0 (0)	0 (0)	0 (0)	0.12 (0.25)
SO_2	2.3 (4.6)	0.9 (1.8)	0.3 (0.6)	1.2 (2.4)	0.5 (1.0)	0.6 (1.2)	0.8 (1.6)	--	2 (4)
Particulates	2.8 (4.6)	2.7 (5.4)	3.0 (6.0)	3.6 (7.2)	1.5 (3.0)	1.8 (3.6)	2.6 (5.2)	--	5.1 (10.2)
NO_x	21.9 (43.8)	27.1 (54.2)	7.2 (14.4)	19.2 (38.4)	3.4 (6.8)	3.4 (6.8)	8.9 (17.8)	--	21.9 (43.8)
Others				NaI 0.2 (0.4) CO 0-0.05 (0-0.1)	CO 0-0.05 (0-0.1)	NaI 0.2 (0.4) CO 0-0.05 (0-0.1)	--	Organic Vapors	HCl 10
Water									
BOD	7 (14)	7.1 (14.2)	2 (4.0)	1.0 (2.0)	0.7 (1.4)	1.0 (2.0)	0	1.0 (2.0)	0
TSS	15 (30)	13.2 (26.4)	8.0 (16.0)	2.8 (5.6)	2.8 (5.6)	2.8 (5.6)	0	2 (4)	0
Color*	--	--	--	Lower	Lower	Lower	0	Lower	0
Toxicity*	--	Lower	Lower	Lower	Lower	Lower	0	Lower	0
Solid* Wastes		Similar	Similar	Lower	Lower	Lower	Little	Similar	Lower
Purchased Energy Requirements KKcal/t	1349	1268	2501	1548	740	951	1456	Unknown	1050
(1000 BTU/Ton)	(4857)	(4566)	(9006)	(5574)	(2665)	(3424)	(5243)		(3781)
Power boiler Capacity KKcal/t	492	492	2401	834	740	951	1237	Unknown	198
(1000 BTU/Ton)	(1772)	(1772)	(8646)	(3003)	(2665)	(3424)	(4454)		(713)

*Compared to kraft mill discharges.

SECTION 3

RECOMMENDATIONS

Development and implementation of several of the new pulping technologies will significantly reduce the amount of both air and water pollution from new mills as well as their energy requirements. A long range research and development program should be implemented to bring those new pulping technologies which are advantageous to the environment and have lower energy requirements into industrial practice.

The processes having the greatest potential for reducing overall pollution are chlorine dioxide pulping and oxygen delignification following high pressure thermomechanical pulping. Halogen pulping has no effluent and manageable air pollution problems. The air pollution problems could be reduced by lower yields or using supplemental fuels in the recovery furnace instead of in separate power boilers.

There would be no toxic materials discharged from a halo pulping mill. Halo pulping, once developed, should receive rapid and wide spread acceptance by the pulping industry because of the high strength pulp produced.

To achieve commercial development of the halo pulping process several problems need to be resolved. Halogen pulping processes need to be further investigated to reduce fiber damage in the refining stage. A high termperature thermomechanical stage to reduce fiber damage should be investigated. A cost analysis of a halo pulp mill should be prepared to determine if the process is economically viable. Energy requirements for production of pulping chemicals should be scrutinized.

Oxygen delignification following high pressure thermomechanical delignification shows the most promise as a pollution free, low energy consuming pulping process. Although the process evaluation in this paper shows a water discharge from the process, this discharge could be eliminated by the development of the appropriate technology. The only discharge arises from the bleach plant. Recycling bleach plant wastes back through the recovery furnace would eliminate all discharges but result in a buildup of chlorides in the cooking chemicals. Chlorides could be removed from the pulping chemicals by crystallizing sodium carbonate from a white liquor side stream and returning the solid to the process, and using the chloride containing stream for bleach plant chemical production. The additional energy gained from the organic materials in the bleach plant effluent may reduce mill energy requirements and result in less air pollution from power boilers.

Work yet required for commercialization of the thermomechanical-oxygen

pulping system is optimization of the thermomechanical stage to result in the least fiber damage, optimization of the oxygen stage to result in the least carbohydrate degradation, development of oxygen stage configuration, and development of a process to dispose of bleach plant wastes in the chemical recovery system.

SECTION 4

KRAFT PULPING

Comparison of non-sulfur pulping processes to existing kraft mills is not a valid comparison. The non-sulfur pulping mills, as well as any new kraft mills, will be built with environmental limitations and energy conservation in mind. To reach a fair assessment of the comparative pollution loads of non-sulfur pulping to kraft pulping, the comparisons should be between mills employing the latest technology. For that reason, a model of a new kraft mill designed with pollution control and energy conservation in mind is used for comparative purposes.

Some of the major new features in a new kraft mill would be, for air pollution control, black liquor oxidation and lime kiln mud oxidation; for water pollution control, use of the decker effluent for brown stock washing and counter current wash in the bleach plant. All new pulping processes will likely use counter current washing in the bleach plant. Figure 1 is a diagram of a kraft mill.

AIR EMISSIONS

Much work is being done to further the state-of-the-art on air emission control. Use of the new control technologies can reduce present day emission levels. The following air pollution estimates are made assuming up to date control technology is being used.

Reduced Sulfur

Reduced sulfur emissions come from three main sources, digestor relief and blow gases, lime kiln exhaust, and black liquor burning. Other minor sources are from washers, black liquor oxidation towers, smelt dissolving tanks, black liquor evaporation, and the lime kiln slaker vent.

Non-condensible gases from digestor relief and flash can be incinerated in the recovery furnace or lime kiln. Reductions in odors from black liquor evaporation and incineration can be reduced by black liquor oxidation. Odors from washers can be eliminated by using diffusion washers. Lime kiln exhaust odors can be reduced by oxidation of the lime mud. New point source standards for new kraft mills require that total reduced sulfur emissions be less than 0.12 Kg/t (0.25 lb/T).

Sulfur Dioxide

Sulfur dioxide emissions from a kraft recovery boiler depend upon the operating conditions of the boiler. High sulfidities, low firing rates, low

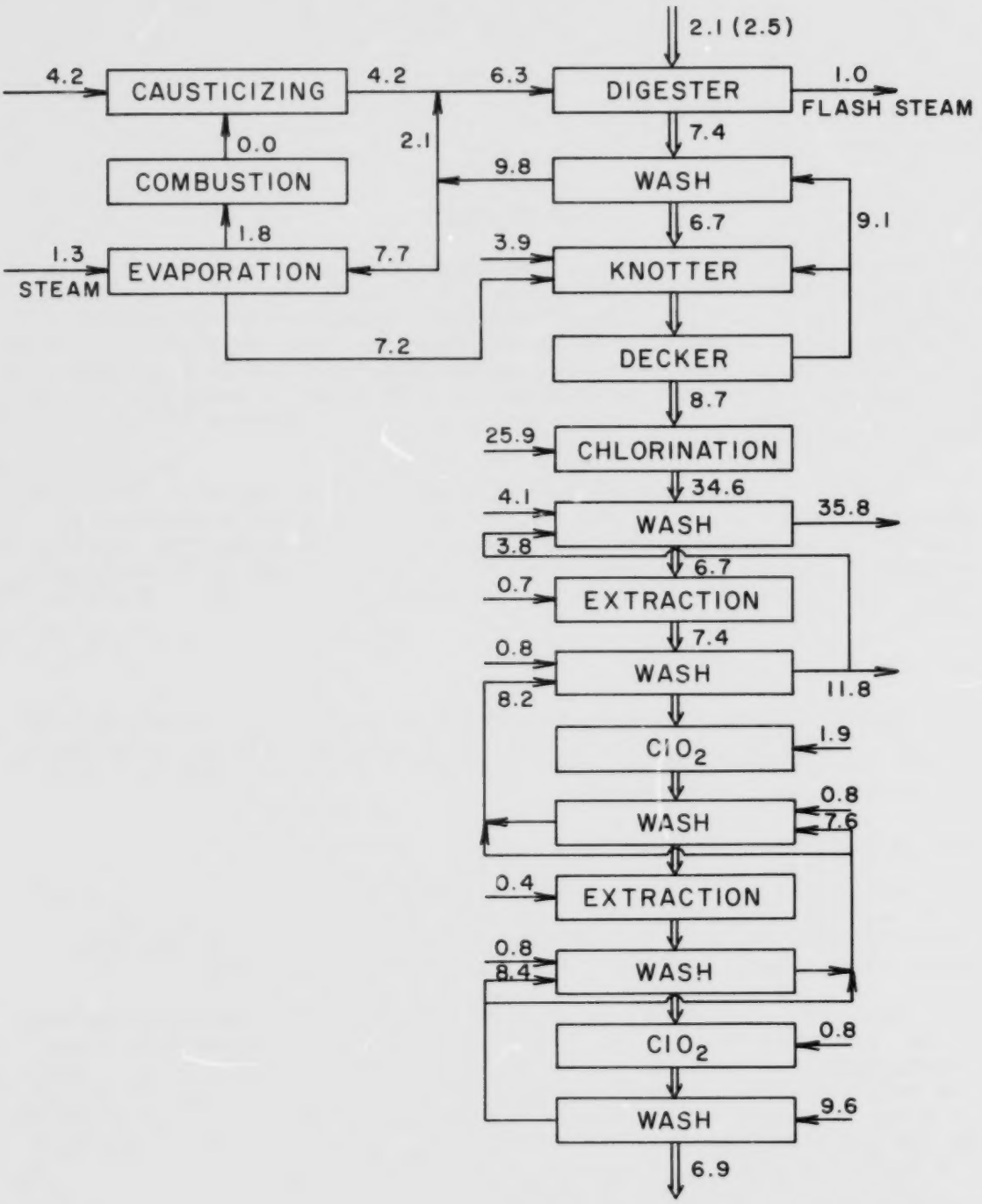

Figure 1. Diagram of a kraft pulping process

bed temperatures, and low primary air temperature will result in high sulfur dioxide emissions. The opposite conditions will result in low or no sulfur dioxide emissions from the recovery boiler. In a new or existing kraft mill these variables can be controlled to minimize sulfur dioxide emissions (2) (3).

Other SO_2 emissions are from the lime kiln and from power boilers. Lime kiln SO_2 emissions are between 0 to 1.4 kg/t (2.8 lb/T), depending upon the sulfur content of the fuel oil (46). Power boiler SO_2 emissions calculated in appendix B are 0.3 kg/t (0.6 lb/T). Total SO_2 emissions from a kraft mill are between 0.3 to 1.7 kg/t (0.6 to 3.4 lb/T).

Particulates

Particulate emissions occur wherever there are combustion processes, particularly (excuse the pun) from the recovery boiler, lime kiln, and power boilers. Incidental emissions of 0.01 to 0.5 kg/t (0.02-1.0 lb/T) occur from the smelt dissolving tank. Particulate emissions from the recovery furnace can be controlled to 2.3 kg/t (4.7 lb/T), and emissions from the line kilns to 0.5 kg/t (1.0 lb/T) (31). Particulate emissions from the power boilers calculated in Appendix C are 0.52 kg/t (1.04 lb/T). Total particulate emissions from a bleached kraft mill are 3.3 kg/t (6.6 lb/T) bleached pulp.

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D, and are 21.9 kg/t (43.8 lb/T) for a kraft mill.

WATER DISCHARGES

Estimates for the BOD and total suspended solids discharges from a kraft mill were taken from BPCTCA Effluent Limitations for the Bleached Kraft Industry (4). The maximum 30 day average for bleached kraft BOD is 7.1 kg/t (14.2 lb/T), and the maximum 30 day average for suspended solids is 12.9 kg/t (25.8 lb/T). Newly built mills should achieve at least half these values through planning for better pulp washing and spill containment.

Color

Color in a kraft mill effluent arises mainly from black liquor spills, decker effluents, and caustic stage bleach plant effluents. In a well designed new kraft mill, black liquor spills should be eliminated or drastically reduced and decker effluents recycled back to brown stock washing. Bleach plant effluents would contain about 140 color units (5).

Toxicity

Toxicity in kraft mill effluents is largely attributed to the fatty acids and to chlorinated lignin fragments in the bleach plant effluent. Fatty acids should be of minor concern in a well designed kraft mill because of a lack of spills and lack of decker effluent. Bleach plant toxicity would remain at about 0.9 toxicity units (5).

SOLID WASTES

Solid wastes from a kraft mill occur from 4 main sources: process losses including wood preparation, green liquor dregs, washing and screening losses, bleach plant wastes, drying wastes and spills; water treatment sludges; fly ash; and biological solids developed from treatment of effluents.

Process losses can be estimated by assuming they are 90% of the raw waste load suspended solids, or that which would be removed in the primary clarifier. Knots and shives are not included because they can be refined or repulped. Process loss solid wastes are estimated to be 22 kg/t (44 lb/T) (6). Water treatment waste solids depend upon the quantity and quality of water treated. The variables are too numerous to attempt an estimate of solids from that source. Fly ash generation will depend upon the quantity of energy required and the type of fuel used in the boiler. Bark and coal will produce the greatest quantity of fly ash, whereas gas or oil will produce none.

Biological solids derived from secondary treatment of effluents are the largest solid waste disposal problem. They have a high volume to dry weight ratio when wet and are difficult to dewater. The quantity of biological solids produced depends upon the quantity and quality of the effluent and the detention time of the secondary treatment. Activated sludge systems will produce more solids than will an aerated lagoon.

ENERGY

The major energy uses in a kraft mill are pulping, evaporation, brown stock washing, bleaching, and lime production. Most of the energy used in a kraft mill is derived from burning the black liquor which contains dissolved wood materials. Appendix A gives calculations for deterimining energy use for a kraft mill.

A new kraft mill would keep its energy requirements low by recycling as much water as possible. In older kraft mills much process heat is used once in heating fresh water, and then discharged. Recovery of low temperature waste heat may be designed into new mills.

The total energy required from external sources in a kraft mill is 1349 KKcal/t (4856 x 10^3 BTU/T). Of that energy required, 852 KKcal/t (3067 x 10^3 BTU/T) is used for causticizing lime mud, and 492 KKcal/t (1771 x 10^3 BTU/T) is used for producing electricity or process steam.

SECTION 5

SODA PULPING

PROCESS DESCRIPTION

Alkaline pulping originally used sodium hydroxide as the active pulping chemical. Small amounts of sulfur compounds found their way into the cooking chemical system so that the original soda mills had a sulfidity of around 5% or less. It was found that the presence of the sulfide in the cooking liquor improved the yield and strength of the pulp. The kraft industry developed when Dahl used sodium sulfate as the make-up chemical in place of soda.

The equipment and processes used in soda pulping are essentially the same as that used in the kraft industry. A model of a soda pulping mill was developed by using a typical kraft type process without use of sulfur compounds.

Chips at 45% moisture are pulped to a 47% yield using 18% chemical on wood and at a liquor to wood ratio of 3:1 in a continuous digestor. The cooking chemical is sodium hydroxide. The pulp is washed counter currently using water from the knotters. The pulp is then bleached in a CEH sequence. Bleaching losses are assumed to be 8%. The black liquor is evaporated and burned in a recovery furnace. The resulting green liquor is causticized. Figure 2 is a block diagram of the model mill.

Some work is being done using potassium hydroxide as the base in place of sodium hydroxide. Potassium hydroxide is a more selective pulping agent than sodium hydroxide and, therefore, produces greater yields (7). If potassium hydroxide is to be used in a mill, washing efficiency of the pulp will have to be greatly increased to reduce losses of cooking chemicals. Potassium hydroxide is considerably more expensive than sodium hydroxide or sodium sulfate.

Recent work has shown that with a 0.1 to 1% anthraquinone addition to soda pulping liquors an increase in pulp yields of a given liquor content can be achieved (8,g). There is insufficient information available as to whether higher pulp strengths can be achieved. If higher pulp strengths can be achieved, anthraquinone could be used to replace sulfur in existing kraft mills to keep odors under control.

Bleached soda pulps are normally used in specialty papers such as offset, book, bond, memo, duplicator, tablet, writing, and envelope grades. Soda pulp strength characteristics are weaker than those of sulfite pulps but have desirable properties of high bulk, good formation, high opacity, high degree of softness, and a smooth surface. The advantage of soda pulping over sulfite pulping is that the soda process can pulp resinous soft woods whereas the

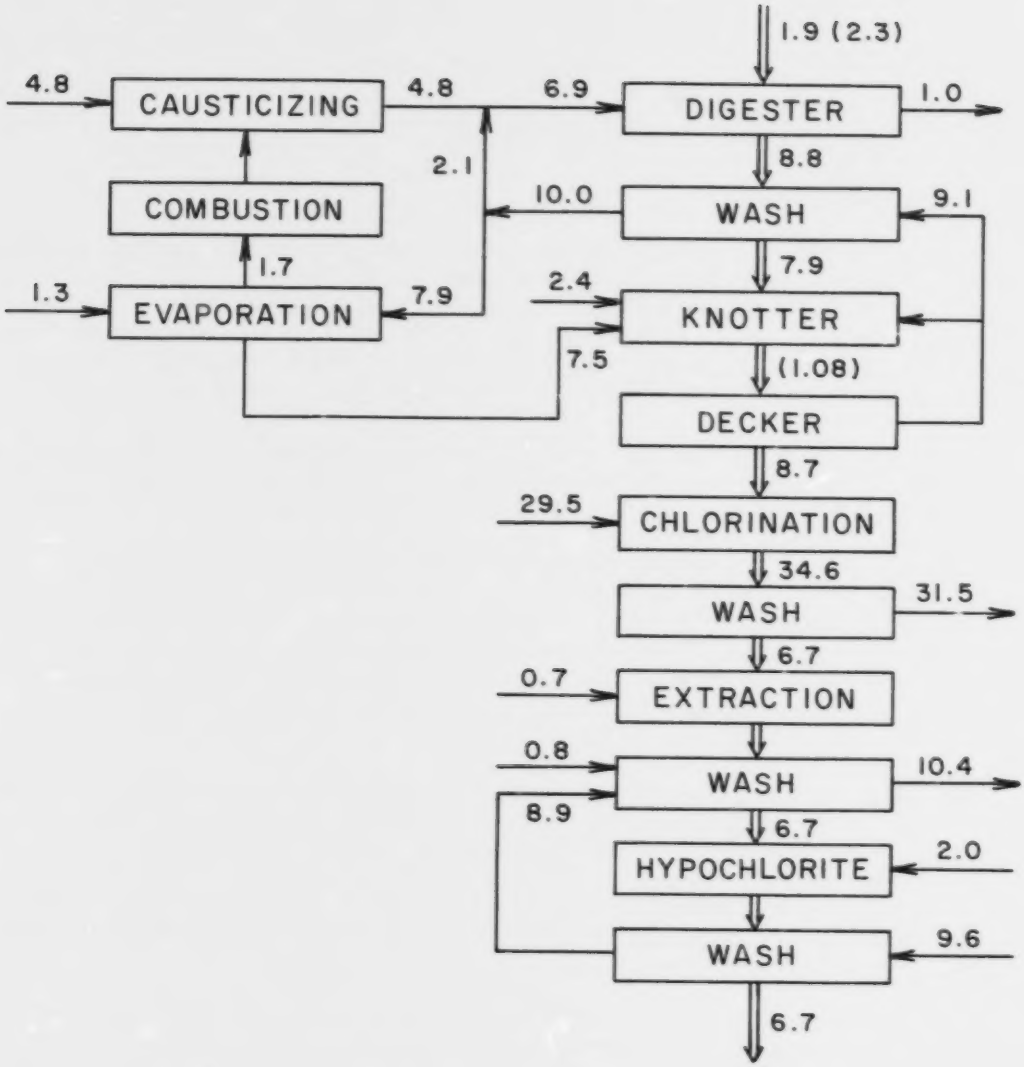

Figure 2. Diagram of a soda pulping process

sulfite process cannot. Soda pulping may be able to compete with the sulfite pulp market, but would be unable to compete with the kraft pulp market due to inferior strength properties. There are presently three mills making pulp from wood chips in the United States. Mills pulping other materials than wood often use a soda cook.

AIR EMISSIONS

Reduced Sulfur Compounds

The lack of sulfur as a pulping chemical allows emissions from a soda pulping mill with greatly reduced odor compared with kraft. Some reduced sulfur odors do occur because of an unintentional buildup of sulfur in the cooking chemical cycle. The sulfur compounds are converted to their reduced state in the recovery furnace. The reduced sulfur compounds are then emitted to the air at various localities in the mill. A number of sources contribute sulfur to a soda pulping mill. Appendix E discusses the sulfur contributions to and escapes from non-sulfur pulping processes.

Uncontrolled reduced sulfur emissions are about 0.01 kg/t (0.02 lb/T). Odors from a soda mill can be effectively controlled by chemically scrubbing the gases containing malodorous compounds with oxidants. Controlled emissions would be about 0.0002 kg/t (.0004 lb/T) reduced sulfur compounds.

Sulfur Dioxide

There should be no sulfur dioxide emissions from the recovery boiler at a soda mill. Small amounts of sulfur dioxide form in the recovery boiler at the low sulfidities present in a soda pulp mill. The sulfur dioxide reacts with sodium carbonate fumes and oxygen is completely removed as sodium sulfate in the electrostatic precipitator.

Sulfur dioxide can be expected in the lime kiln flue gas. The quantity present will depend upon the sulfur content of the fuel and the quantity of CaO required. About 60% more NaOH on wood is required for soda pulping than for kraft pulping. Therefore, soda mills should emit about 60% more SO_2 from their lime kilns than do kraft mills. Sulfur dioxide from the lime kiln will range between a trace and 0.32 kg/t (.64 lb/T) (10).

Sulfur dioxide will be present in the power boiler fuel gas. The quantity present will depend upon the sulfur content of the fuel and the amount of steam required by the mill. Power boiler capacities required to operate a soda pulping mill are calculated in Appendix A. Appendix B shows sulfur dioxide emission calculations from power boilers for different fuels. Sulfur dioxide emissions from power boilers based on the use of wood wastes are used in the summation of the total mill SO_2 emissions because wood wastes are the lowest cost fuel. SO_2 emissions from the power boiler are 0.3 kg/t (0.6 lb/T) pulp.

A soda pulping mill will emit approximately 0.94 kg/t (1.88 lb/T) pulp sulfur dioxide.

Particulates

Particulate emissions from the soda process are shown in Appendix C. They are much higher than kraft particulate emissions because sodium hydroxide and sodium oxide volatilize at a considerably lower temperature in the recovery furnace than does sodium sulfide and sodium sulfate. These volatilize at a considerably lower temperature in the recovery furnace than does sodium sulfide and sodium sulfate. These volatilized sodium compounds condense and react with flue gases to form particulates. In summary, emissions are: from the recovery furnace, 1.55 kg/t (3.0 lb/T) pulp; from the smelt tank, 0.25 kg/t (0.54 lb/T) pulp; and from the lime kiln, 0.5 kg/t (1.0 lb/T) pulp; from the power boiler, 0.5 kg/t (1.0 lb/T) pulp, for a total of 2.8 kg/t (5.2 lb/T) pulp.

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D and are 21.1 kg/t (42.2 lb/T) for a soda pulping mill.

WATER DISCHARGES

The major effluent sources from a soda pulp mill are decker seal pit water, digestor relief condensates, evaporator condensates, bleach plant effluent, spills, and miscellaneous wastewaters including recovery plant discharge, boiler plant blowdown and water treatment wastes. Pollutional compounds present are BOD, suspended solids, color, and toxicity.

Biochemical Oxygen Demand

Raw waste BOD values from soda mills range between 20 and 30 kg/t (40-60 lb/T) of pulp produced. Half of the BOD originates from the bleach plant (11). After treatment the maximum 30 day average BOD values will be less than 7.1 kg/t (14.2 lb/T), which is the Best Practicable Control Technology Currently Available effluent guidelines limitation for the soda subclassification.

Total Suspended Solids

Raw waste total suspended solids from a soda mill range between 20 and 30 kg/t (40-60 lb/T) of pulp produced (11). Solids in the raw waste are removed sufficiently in primary and secondary treatment and have little effect on the treated effluent. Suspended solids are generated by biological treatment. Suspended solids after treatment are less than 13.2 kg/t pulp (26.4 lb/T), the Best Practicable Control Technology Currently Available effluent guidelines limitation for the soda subcategory.

Color

Little information on color discharges from soda mills is available.

Toxicity

Soda pulping effluents contain compounds that are toxic to aquatic life. Toxic compounds contained in soda mill effluents are resin acid soaps and turpene derivatives. Since sulfur is not used in the process the effluents appear to have a slightly lower toxicity level than kraft mill effluents (5) Another paper reports that soda mill white water is considerably less toxic than kraft mill white water (12).

SOLID WASTES

Solid wastes from a soda mill occur from 4 main sources: 1) process losses including wood preparation, green liquor dregs, washing and screening losses, bleach plant wastes, drying wastes and spills; 2) water treatment sludges; 3) fly ash; and 4) biological solids developed from treatment of effluents.

Process losses can be estimated by assuming they are 90% of the raw waste load suspended solids, or that which would be removed in the primary clarifier. Knots and shives are not included because they could be refined or repulped. Process loss solid wastes are estimated to be 22 kg/t (44 lb/T) (6). Water treatment waste solids depend upon the quantity and quality of water treated. The variables are too numerous to attempt an estimate of solids from that source. Fly ash generation will depend upon the quantity of energy required and the type of fuel used in the boiler. Bark and coal will produce the greatest quantity of fly ash, whereas gas or oil will produce none.

Biological solids derived from secondary treatment of effluents are the largest solid waste disposal problem. They have a high volume to dry weight ratio when wet and are difficult to dewater. The quantity of biological solids produced depends upon the quantity and quality of the effluent and the detention time of the secondary treatment. Activated sludge systems will produce more solids than will an aerated lagoon. Overall, a soda mill will produce about the same quantity of solids as a kraft mill.

ENERGY

The energy use in a soda mill is quite similar to that found in a kraft mill. There are two major differences; the amount of energy produced in the recovery furnace is greater for soda mills than for kraft mills, and a soda mill uses more fuel oil in the lime kilns. Kraft mills produce less energy in the recovery furnace than do soda mills because large quantities of energy are required to reduce sulfates to sulfides. Soda mills have no sulfur compounds in their cooking liquors. The sulfide in kraft mill liquors supplies some of the active alkali during digestion. Because of the lack of sulfides in a soda mill more sodium hydroxide is required to provide the active alkali and more lime is required for caustization of the green liquor.

The soda process requires a total purchased energy of 1268 KKcal/t (4,566 KBTU/T) bleached pulp. Of that energy, 1117 KKcal/t (4,022 KBTU/T)

is contained in fuel oil to fire the lime kiln. The remaining 151 KKcal/t (544 KBTU/T) will most likely be produced by burning bark and wood residues.

SECTION 6

SODA SEMICHEMICAL PULPING

PROCESS DESCRIPTION

Semichemical pulping was developed to produce high yield chemical pulps. The chips are cooked in a digestor with chemicals for a shorter time than a full chemical cook, then are refined to produce pulp. Most semichemical pulping uses neutral sulfite pulping chemicals.

A model of a soda semichemical pulp mill was used to calculate pollution loads and energy requirements. Chips at 45% moisture are pulped to a 75% yield in a continuous digestor. PUlping conditions were: 10% chemical on wood, 3:1 liquor to wood ratio, and 20% NaOH and 80% Na_2CO_3 as chemical on wood. The cooking temperature was 170°C (338°F). After blowing the chips are passed through a refiner, then washed and screened. If the pulp is to be used for making paper it is bleached in a CEH sequence. The black liquor is evaporated and burned. The resulting green liquor is partially causticized. The process is shown in Figure 3.

Pulp Properties and Uses

The pulps produced are similar to those produced by NSSC. These pulps are most suitable for production and corrugating media, braille, duplicator, envelope, ledger, and offset type papers where high strengths are not required.

State of Development

Many mills producing semichemical corrugating medium by the NSSC process are converting to sulfur free processes. Eight mills made the conversion in 1977 and four more are considering the change (13). The conversion is being made for three reasons. 1) poor markets for the salt cake by-product produced by NSSC pulping via fluidized bed incinerators; 2) high chemical costs because sodium sulfate and soda ash can not be recycled and 3) reduced sulfur emissions leading to odor problems.

AIR EMISSIONS

Reduced Sulfur Compounds

The lack of sulfur as a pulping chemical greatly reduced odor emissions from a soda semichemical pulping mill. Some reduced sulfur odors do occur because of an unintentional build up of sulfur in the cooking chemical cycle.

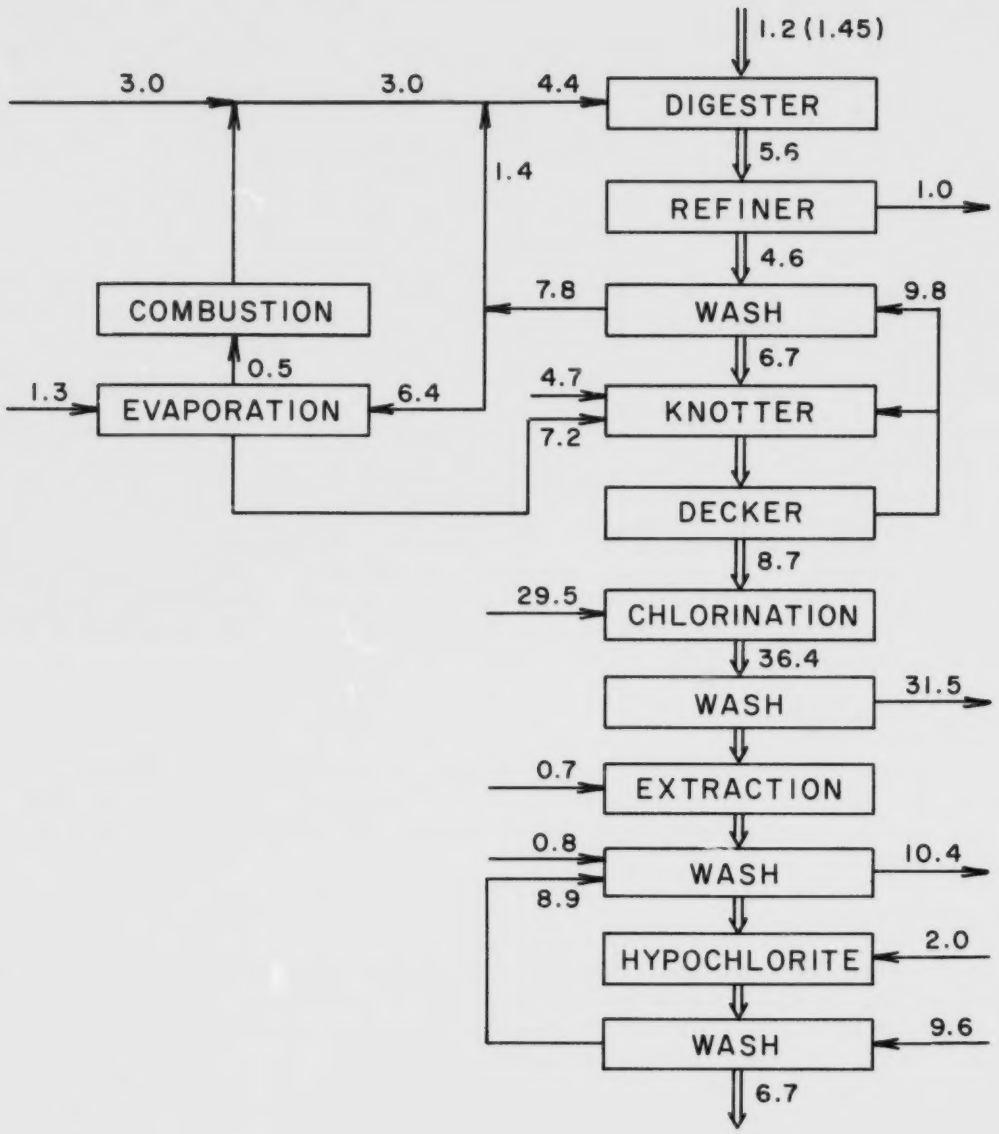

Figure 3. Diagram of a soda semichemical pulping process

The sulfur compounds are converted to their reduced state in the recovery furnace. A number of sources contribute sulfur to a soda pulping mill. Appendix E discusses the sulfur contributions and losses in non-sulfur pulping processes.

Uncontrolled reduced sulfur emissions are about 0.01 kg/t (0.02 lb/T). Odors from a semichemical soda mill can be removed by chemically scrubbing the gases containing malodorous compounds with oxidants. Controlled emissions would be about 0.0002 kg/t (.0004 lb/T) reduced sulfur compounds.

Sulfur Dioxide

There should be no sulfur dioxide emissions from the recovery boiler at a soda semichemical mill. Small amounts of sulfur dioxide that form in the recovery boiler at low sulfidities react with sodium carbonate fumes and are removed as sodium sulfate in the electrostatic precipitator.

Sulfur dioxide can be expected in the lime kiln flue gas. The quantity present will depend upon the sulfur content of the fuel and the quantity of CaO required. Since the cooking liquor Na_2CO_3 to NaOH ratio is between 2:1 and 4:1, and 10% Na_2O on wood is used (14), much less calcium oxide is required than in a kraft mill. A kraft mill needs to produce 188 kg (376 lb/T) CaO per ton of pulp. A semichemical soda mill will require less than 47 kg (97 lb/T) CaO per ton pulp, or about 25% of a kraft mill lime requirement. Sulfur dioxide emissions from the lime kiln would be between a trace and 0.05 kg/t (0.10 lb/T). These values were computed by taking 25% of emissions expected from a kraft lime kiln.

Sulfur dioxide will be in the power boiler flue gas. The quantity present will depend upon the sulfur content of the fuel used and the amount of steam required by the mill. Appendix B shows that SO_2 emissions from a soda semichemical mill to be about 0.5 kg/t (1.0 lb/T) pulp for oil fired boilers, 0.8 kg/t (1.6 lb/T) pulp for coal fired boilers, and 0.3 kg/t (0.6 lb/T) for waste wood fired boilers.

Particulates

Particulate emissions from the soda semichemical process are shown in Appendix C. In summary, emissions are: from the recovery furnace, 0.29 kg/t (0.38 lb/T) pulp; from the smelt tank, 0.1 kg/t (0.2 lb/T) pulp; from the lime kiln, 0.11 kg/t (0.22 lb/T) pulp; and from the power boiler, 3.0 kg/t (6.0 lb/T) pulp, for a total of 3.5 kg/t (7.0 lb/T) pulp.

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D and are 7.2 kg/t (14.4 lb/T) for a soda semichemical pulp mill.

WATER DISCHARGES

The major effluent sources from a soda semichemical pulp mill are decker seal pit water, digestor relief condensate, bleach plant wastes, spills, and

miscellaneous waste water including recovery plant discharge, boiler plant blowdown, and water treatment plant wastes.

Biochemical Oxygen Demand

Raw waste loads from a soda semichemical pulping mill are about 18-19 kg BOD per t (36-38 lb/T) pulp (11). Nearly 80% of this BOD comes from the pulp mill consisting largely of digestor relief condensate and spills. The remaining 20% comes from carryover in the evaporators. The BOD is reduced to 2 kg BOD per t (4 lb/T) pulp with biological treatment.

Total Suspended Solids

Raw waste total suspended solids from a soda semichemical mill are about 40 kg/t (80 lb/T) pulp (11). About 60% of the suspended solids come from the pulping area, largely from spills. The remaining 40% of the suspended solids come from the liquor recovery area and water plant discharges (15). Solids in the raw waste are removed sufficiently in primary and secondary treatment and have little effect on the solids discharged. Suspended solids are generated by biological treatment and make up the bulk of the solids in the discharge. Suspended solids discharge from this type of mill is estimated to be 8 kg/t (16 lb/T) pulp. This estimate was arrived at by dividing the BOD from a soda mill by the ratio of BOD in the inlet to the suspended solids in the effluent from a kraft mill.

Color

Little information on color discharges from a soda semichemical mill is available.

Toxicity

Soda mill effluents are reported to be less toxic than kraft mill effluents (12). Toxic materials such as dimethyl sulfide are not present, although the resin acids are.

SOLID WASTES

Solid wastes from a semichemical soda mill occur from 4 main sources: process losses including wood preparation, green liquor dregs, washing and screening losses; drying wastes, and spills; water treatment sludges, fly ash; and biological solids developed from treatment of effluents. Process losses can be estimated by assuming they are 90% of the raw waste load suspended solids, or that which would be removed in the primary clarifier. Knots and shives can be refined or repulped to reduce solids loss. Process loss solid wastes are estimated to be 36 kg/t (72 lb/T). Water treatment waste solids are dependent upon the quantity and quality of water to be treated. The variables were too numerous to attempt an estimate. Fly ash generation will depend upon the quantity of energy required and the type of fuel used in the boiler. Bark and coal will produce the greatest quantity of fly ash, whereas gas and oil will produce none. Biological solids derived from secondary treatment of effluents are the largest solid waste disposal problem.

They have a high volume to dry weight ratio when wet and are difficult to dewater. The quantity of biological solids produced depends upon the quantity and quality of the effluent and the detention time of the secondary treatment. Activated sludge systems will produce more solids than will an aerated lagoon. Overall, a soda mill will produce about the same quantity of solids as a kraft mill.

ENERGY

Energy requirements for the various pulping processes are calculated in Tables 6 through 16 in Appendix A. Energy requirements from sources external to the mill are 91 KKcal/t pulp (328 KBTU/T) for causticizing and 2401 KKcal/t pulp (8646 KBTU/T) for other mill power requirements for a total of 2501 KKcal/t (9006 KBTU/T) pulp. Electrical energy is assumed to be produced on site from high pressure steam from either the recovery furnace or auxiliary power boiler. Either gas, oil, or coal was assumed to be burned in the auxiliary power boiler.

Purchased energy requirements per ton pulp in a soda semichemical mill are high because of the high yield. High yield results in less organic materials to be burned in the recovery furnace and thus in less energy production. A semi-bleaching sequence saves some energy.

SECTION 7

OXYGEN ALKALI PULPING

PROCESS DESCRIPTION

Oxygen pulping is being developed as a means of producing a high strength chemical pulp without the odor problems associated with the kraft pulping process. Oxygen alkali pulping is essentially a soda pulping process followed by an oxygen delignification or oxygen bleach stage. The combination of the soda pulping and oxygen delignification yields a pulp suitable for bleaching by a DED sequence.

Comparison of Process Alternatives

Yield

In oxygen-soda pulping delignification takes place in two stages, in the soda stage and in the oxygen stage. The relative amount of delignification occurring in each stage has a strong effect upon the pulp strengths when compared at the same overall final yield. Pulps produced with a low amount of delignification in the soda stage and the major portion of delignification in the oxygen stage produced low strength pulps and required long detention times in the oxygen stage (16). Pulps produced by delignification to the fiberization point in the soda stage and further delignification in the oxygen stage produced the strongest pulps (17) (18). For purposes of pollutant calculations in this paper a soda yield of 55% and a soda-oxygen yield of 50% were assumed. An additional 5% yield loss during bleaching was also assumed.

Cooking Conditions

To achieve a full chemical pulp in the soda stage sodium hydroxide is required. Pulping with $NaHCO_3$ results in a high shives content (19). The chips are cooked with 8-13% NaOH as Na_2CO_3 on wood depending on the yield desired (16), (17), (20), (21). 16% NaOH on wood in the soda stage was used for the calculations in this paper. The liquor to wood ratio was assumed to be 3:1 in the soda stage. The cook temperature was assumed to be 160°C.

Sodium hydroxide, sodium carbonate, and sodium bicarbonate have been investigated for use as active alkali in the oxygen stage. The active alkali acts primarily as a buffering agent in oxygen delignification (18). High pH's lead to excessive degradation of the cellulose while low pH's result in slow reaction rates. The pH should ideally be held between 8.0 and 9.5. Production of organic acids and carbon dioxide by the oxidation reactions results in consumption of active alkali.

Addition of NaOH at once causes too high an initial pH. The addition of Na_2CO_3 results in a satisfactory oxygen cook. The pH of the cook can be controlled by the digestor relief rate, that is by control of the CO_2 content of the gases (22).

Alkali dosages above 7% are reported to result in weak pulps (17). An alkali dosage of 5% was used in the oxygen stage. Oxygen consumption has been reported to be 15 to 18% on the soda stage pulp (16). Bleed off of gases produced during delignification will result in a loss of oxygen, bringing the oxygen requirement to 20 to 30% of the weight of wood. The consistency in the oxygen stage was assumed to be 10%. Oxygen consumption will increase with higher recycle rates of black liquor to the digestor due to oxidation of black liquor solids. This will also result in a loss of heating value of the black liquor (23).

In choosing a temperature in the oxygen stage the degradation of cellulose must be balanced by delignification rate or reactor size. At oxygen stage temperatures above 120°C (248°F) to 140°C (284°F) the pulp strength properties deteriorate rapidly (17). At lower temperatures the delignification rate drops off rapidly. For the calculations, 120°C (248°F) was used. Figure 4 shows the process.

Products

Oxygen pulps can be used in the same applications as kraft pulps except where tear and fold are critical. Oxygen pulps typically have low tear and fold properties. Oxygen pulps would be well suited to use as linerboard. They may also be used in register, bond, and memo papers. Tissue could not be made from oxygen pulp because of the low tear.

State of Development

The first full scale mill using soda pulping followed by oxygen delignification has just been built and is presently going through start up and shake down. No details are available to date about the mill and its characteristics. If this mill is a commercial success, more pulping mills of the soda-oxygen type may be expected in the future.

AIR EMISSIONS

Reduced Sulfur Compounds

Oxygen pulping mills are not entirely sulfur free and therefore the possibility of reduced sulfur odor emissions exists. Although all sulfur present in the oxygen stage will be in the oxidized form, reduced sulfur compounds will be present at other locations in the mill. The soda stage will contain reduced sulfur compounds and could have an odor problem. Appendix E shows possible odor emissions from a soda pulping mill. Since pure oxygen will be available in the mill, small quantities could be introduced into the soda stage to oxidize the sulfur compounds and eliminate odors.

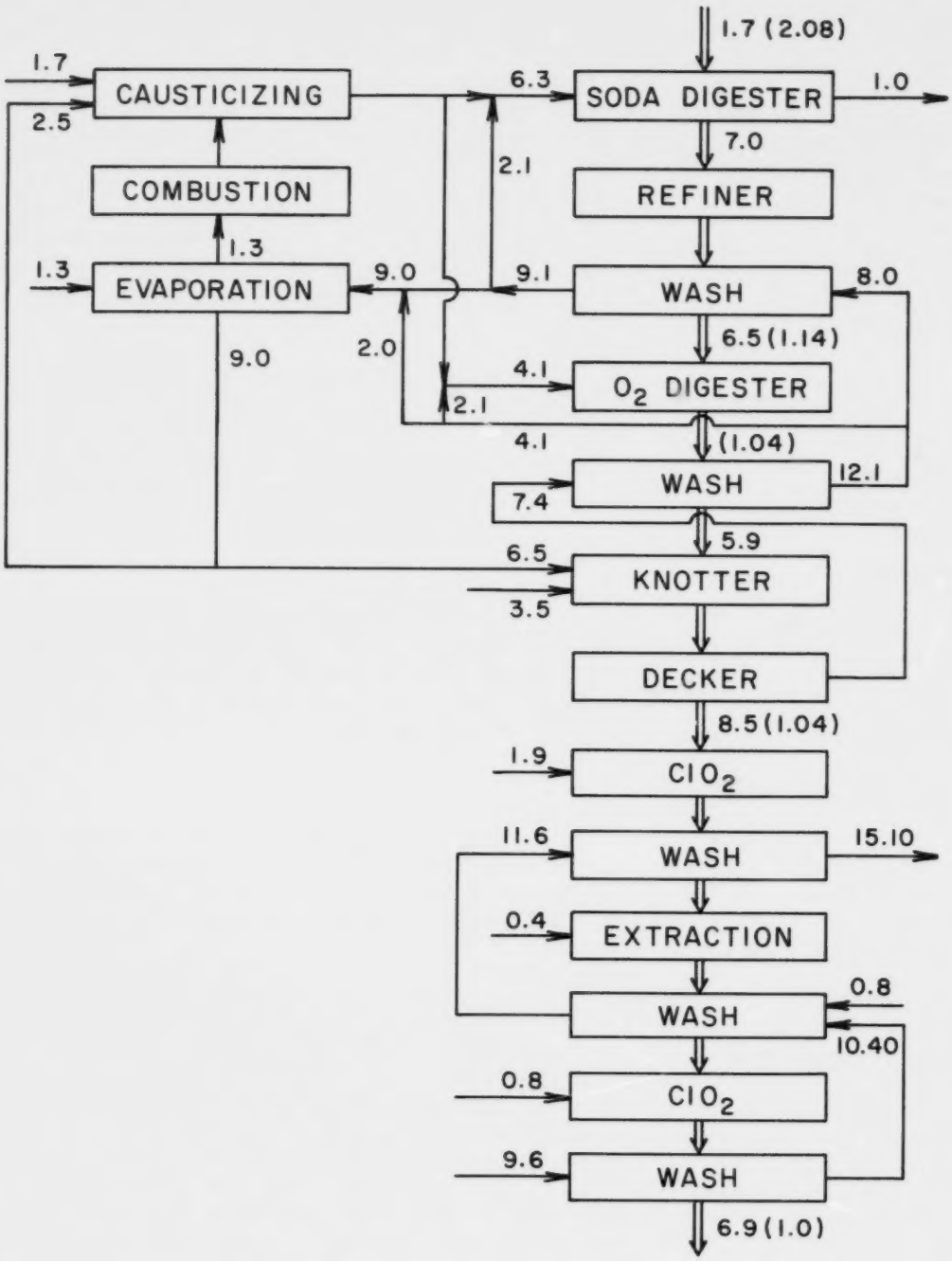

Figure 4. Diagram of an oxygen alkali pulping process

Sulfur Dioxide

There should be no sulfur dioxide emissions from the recovery boiler at an oxygen-soda mill. Small amounts of sulfur dioxide form in the recovery boiler due to the low sulfur content of the pulping liquors. The sulfur dioxide reacts with the sodium carbonate fumes in the flue gas and is removed as sodium sulfate in the electrostatic precipitator.

Sulfur dioxide can be expected in the lime kiln flue gas. The quantity present will depend upon the sulfur content of the fuel and the quantity of CaO required. About 5% more NaOH on wood is required for oxygen-soda pulp than for kraft pulp so SO_2 emissions should be about 5% more than from kraft mills. Emissions will range between a trace to 0.21 kg/t ADP (0.42 lb/T ADP) (10).

Sulfur dioxide will be in the power boiler flue gas. The quantity present will depend upon the sulfur content of the fuel and the amount of steam required by the mill. Calculations for SO_2 emissions from the power boiler are in Appendix B. SO_2 emissions for oil fired furnaces are 2.8 kg/t (5.6 lb/T) pulp; for coal fired furnaces, 4.4 kg/t (8.8 lb/T); and for waste wood fired boilers, 0.6 kg/t (1.6 lb/T) pulp.

Particulates

Calculations for particulate emissions are in Appendix C. Emissions from the recovery furnace are 2.33 kg/t (4.6 lb/T) pulp which includes the contribution due to sodium iodide if iodide is used as a carbohydrate protector during pulping. If sodium iodide is not present, particulate emissions from the recovery furnace would be slightly less. Another contribution to the total particulate emissions from a soda oxygen mill is 0.21 kg/t (0.42 lb/T) from the power boilers. The total particulate emissions from a soda oxygen mill is estimated to be 3.85 kg/t (716 lb/T).

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D and are 19.2 kg/t (38.4 lb/T).

Iodide

If iodide is used as a cellulose degradation inhibitor in the oxygen delignification stage, there is a possibility of iodide emissions from the recovery furnace. Sodium iodide vaporizes at 1304°C (2379°F), well above the bed temperature of a normal recovery furnace of about 982°C (1800°F), however, at 982°C (1800°F) sodium idodide has a vapor pressure of 28 mm Hg, which means a considerable quantity of sodium iodide can be vaporized. Sodium chloride (which has a vapor pressure lower than sodium iodide), is known to readily vaporize from kraft mill recovery furnaces. Condensation of the iodide will form a fume. The fumes can probably be removed from the flue gas via an electrostatic precipitator with other particulates, although electrostatic precipitators are not as efficient on sodium chloride as they are on other sodium salts, and therefore may show a poor performance on sodium iodide.

About 60 kg/t (120 lb/T) NaI on pulp is projected. About 40% of the NaI in the black liquor will be vaporized, of which 50% will be captured in the direct contact evaporator and 98% of the remainder removed by the electrostatic precipitator. NaI emissions would be about .24 kg/t (0.48 lb/T) pulp.

If pulping chemicals are to be recovered by a wet oxidation method, there would be no air emission of sodium iodide (24).

Carbon Monoxide

The formation of carbon monoxide in oxygen bleaching mills has been observed. At low consistencies between 0 to 50 g (0.1 lb/T) carbon monoxide per ton was measured, and at high consistencies (20-30%) 300 to 500 g (0.6 to 1.0 lb/T) carbon monoxide per ton pulp was observed in the degasing line (25). Similar formation of carbon monoxide was found in an oxygen pulping system (26). Carbon monoxide formed during oxygen pulping can be handled by venting the pressure relief gases to the recovery furnace or lime kiln air intake, as is done in kraft mills for odor control. There should be no carbon monoxide emissions allowed from an oxygen pulping mill.

WATER DISCHARGES

New pulp mills will have the advantage of being able to install the newest technology for control of water effluents. Materials of construction can be chosen so that corrosion is minimized. Old equipment would not require modification or need to be replaced and plant layout can maximize the efficiency of recycle. Water pollution discharges will be lower than existing mills, disregarding the oxygen pulping. Oxygen pulping itself offers several advantages, largely that the chlorination and first extraction stages in the bleach plant are no longer required. Nearly 80% of the bleach plant BOD is contained in the chlorination and first extraction stages of the bleach plant.

With new technology such as that used in the Rapson process, chlorides may be removed from the cooking liquor enabling bleach plant effluents to be recycled to the pulping cycle. These mills would have no discharge.

Biochemical Oxygen Demand

BOD discharges from an oxygen pulp mill are much lower than from a kraft mill. Practices that result in reduced BOD are reuse of decker water on the brown stock wash and elimination of the chlorination and first extraction stage in the bleach plant. The evaporator condensate waters are recycled to the screen and causticizing department. The only pollutant from the pulping stage would be from the relief gas concentrate turpentine separation, minor flows from the causticizing department, and from leaks and spills. Digestor condensate from a continuous digestor contains 2.6 Kg/t (5.8 lb/T) BOD (15). Spills and miscellaneous flows may amount to 3 Kg/t (6.0 lb/T) (15).

Bleach plant effluents from an oxygen pulp mill will be much less than that from a kraft mill. The oxygen pulping stage eliminates the need for the chlorine and first extraction step leaving a DED sequence. The largest flow will be from the chlorine dioxide stage wash. BOD from the DED bleaching se-

quence in a kraft mill is between 2 and 3 Kg/t (4-6 lb/T) (27), (28). Raw BOD loadings from an oxygen pulping mill bleach plant will be slightly higher than a kraft mill DED portion of bleach plant because of carry over of black liquor solids from the decker into the bleach plant which are normally washed out in the chlorination stage. BOD loading from an oxygen bleach plant should be about 3 to 4 Kg/t (6-8 lb/T) pulp.

Total BOD raw waste loading from an oxygen pulp mill is about 8.6 to 9.6 Kg/t (17.2-19.2 lb/T) pulp. Assuming a 90% efficient waste treatment system, final BOD discharges will be in the range of .86 to .96 Kg/t (1.72-1.82 lb/T).

Suspended Solids

Because of the reduced discharges due to recovery of decker effluents and short bleaching sequences, suspended solids discharges will be less than expected from a kraft mill. Suspended solids would enter the sewer through spills, lime kiln dregs, water treatment plant sludges, and bleach plant effluents. Spills will contribute about 5 Kg/t (10 lb/T) suspended solids. Causticizing and boiler room effluents will contribute about 3 Kg/t (6 lb/T) suspended solids.

Most of the suspended solids in the raw waste load will be removed by primary and secondary treatment. Solids produced by biological activity during secondary treatment will make up the bulk of suspended solids in the effluent, and is directly related to the BOD and the method of treatment. Assuming a concentration of 100 mg/l suspended solids escaping in the effluent and a flow of 28,000 l/t (1679 gal/T) pulp, suspended solids leaving with the treated effluent are 2.8 Kg/t (5.2 lb/T) pulp.

Color

Oxygen pulping liquors have about one fourth the color of kraft or soda liquors (12), (29). Spills from screening and deckers would thereby contain relatively little color. The strongly colored chlorine extraction stage effluent would also not be present. The DED bleaching effluent has 1.5% of the color of the full CEDED bleaching sequence (5).

Toxicity

Conditions present during oxygen pulping destroy resin and fatty acids that are responsible for toxicity in many pulp mill discharges (30). Other toxic materials such as methyl sulfides are not present because of the absence of reduced sulfur. Bio-assay tests have shown that oxygen pulping liquors are non-toxic (12). The chlorination stage bleach plant effluent which contributes to effluent toxicity is not present in oxygen pulping mills. Chlorine dioxide bleaching effluents have been shown to be less toxic than chlorine stage effluents (5). Toxicities resulting from the bleach plant effluent are shown in Table 2.

TABLE 2. TOXICITY AND COLOR OF BLEACH PLANT EFFLUENTS

Stage	Toxicity Units	Color Units	BOD
C	.5	140	9.0
E	.2	338	7.0
D	.13	7.3	1.9

SOLID WASTES

Solid wastes from an oxygen-soda mill come from several sources: 1) process losses, including wood preparation, green liquor dregs, washing and screening losses, bleach plant wastes, drying wastes, and spills; 2) water treatment sludges; 3) fly ash; 4) and biological solids developed from treatment of effluents.

Process solids losses can be estimated by assuming that 90% of the suspended solids in the effluent are removed in the primary clarifier. Knots and shives are re-refined. Process solids losses are estimated to be 8 Kg/t (16 lb/T) so that clarifier solids to be disposed of are estimated to be 9 Kg/t (18 lb/T). Addition of metal salts to retard cellulose degradation will result in extra green liquor dregs of about 2.0 Kg/t (4.0 lb/T).

Water treatment waste solids are dependent upon the quality and quantity of the water to be treted. Water quality is highly variable, depending upon plant location and season, and thereby making estimates of sludges produced difficult. Water use in an oxygen-soda mill would be less than that of kraft, so the solids produced by this source are less.

Fly ash generation will depend upon the quantity of energy required and the type of fuel used in the boiler. Bark and coal will produce the greatest quantity of fly ash, whereas gas or oil will produce none. Use of external energy is greater for oxygen soda pulping than for kraft, so fly ash generation will be greater.

Biological solids derived from secondary treatment of effluents are the largest solids waste disposal problem. They have a high volume to dry weight ratio when wet and are difficult to dewater. The quantity of biological solids produced depends upon the quantity and quality of the effluent and the detention time of the secondary treatment. Activated sludge systems will produce more solids than will an aerated lagoon. Overall, an oxygen-soda mill will produce less biological solids than a kraft mill because of the lower raw BOD loading to the treatment plant.

ENERGY

The major energy uses in an oxygen-soda mill are for heating the digestors, evaporating the black liquor, bleaching, and causticizing. Digestor

heating is a major energy user because pulping is by a two stage process with washing in between. In each stage high value steam is used to heat the digestors, and hot water is produced when the pulp is blown. A well designed mill should be able to recover this heat for other uses in the mill such as wash water in the bleach plant. Black liquor evaporation uses more energy than other pulping processes because of the high loading to the evaporators. The two digestors in sequence produce more liquors to be evaporated than other processes. To reduce the evaporator energy requirements, higher consistencies can be used in the oxygen stage or a higher degree of black liquor recycle used so as to reduce the evaporator loading.

The amount of energy recovered from burning the black liquor is not as great as in a kraft mill because of the higher unbleached yield and the oxidation of some of the organics in the oxygen pulping stage. Higher yields result in less organic materials to be burned in the recovery furnace. Destruction of organics in the oxygen stage also results in less organics to be burned in the recovery furnace. Oxidation of organics in the digestor liberates heat in the digestor, so digestor heating requirements are reduced. Production of tonnage oxygen consumes energy but is partically offset by a reduction in energy required to produce bleach plant chemicals. The oxygen delignification stage replaces the first chlorination and extraction steps in the bleach plant, realizing energy savings in the bleach plant.

For an oxygen soda pulp mill the energy required from sources external to the mill is 1287 Kcal/t (4634 KBTU/T). Of that energy, 714 Kcal/t (2570 KBTU/T) is required for causticizing and 561 Kcal/t (2020 KBTU/T) is used to fire power boilers.

SECTION 8

THERMOMECHANICAL PULPING FOLLOWED BY OXYGEN DELIGNIFICATION

Process Description

Because oxygen pulping is diffusion limited (20), different means are employed to expose the lignin directly to the pulping liquors. In thermomechanical pulping the chips are reduced to fibers by refining. High temperatures are used to reduce the damage to pulp fibers. The lignin is then readily available to attack by oxygen in the pulping liquor.

Chips are first cooked with steam under high pressure for about 5 minutes, then refined while under pressure. The pulp then passes into the oxygen stage where active alkali and oxygen are added. Following the oxygen stage the pulp is washed, screened, and bleached if desired. The bleaching sequence is DED since the oxygen stage replaces the chlorine and extraction stages of a normal full bleaching sequence. The cooking liquors are evaporated and the solids incinerated for chemical recovery. If NaOH is the pulping chemical, the green liquor passes through a causticizing plant. If $NaCO_3$ is the pulping chemical, the causticizing plant is unnecessary.

Comparison of Process Alternatives

Thermomechanical Stage

The significant process variables in the thermomechanical stage are the cook time, cook temperature, and refiner rpm and clearance. Sufficient time in the preheater is required to raise the chips to a uniform temperature. Less than 5 minutes are required for heating the chips. The preheating temperature governs the amount of lignin softening that occurs.

When wood chips are heated the lignin and hemicelluloses between the cell walls becomes soft. The softening of the lignin begins at specific temperatures referred to as the glass point. The glass point for each species of wood is different. During cooking the lignin is heated to the glass point so the fibers can be easily separated upon refining. At temperatures below the glass point the wood fractures through the outer layer of the secondary cell wall. At temperatures above the glass point the wood fractures through the lignin layers between the cells. When wood has been fiberated above the glass point the fibers will be coated with a layer of lignin (31). The transition between spruce fracturing in the cell wall or fracturing between the cell wall occurs between 120°C (248°F) and 135°C (275°F) (31). The thermomechanical pulps will be stronger if the fibers have not been torn. A thermomechanical stage temperature of 160°C (320°F) was used.

Oxygen Stage

The majority of the delignification takes place in the oxygen stage of oxygen thermomechanical pulping. Critical parameters are time, temperature, active alkali concentration, pH, stirring rate, and oxygen pressure.

The amount of time required in the oxygen stage is a function of all the other parameters mentioned. Pulps with kappa numbers below 15 can be produced in less than 2 hours (32). The time required may be shortened by optimizing the other variables. Stirring, which increases oxygen availability, is of prime importance. The conditions in most laboratory oxygen pulping investigations are that of oxygen starvation. All the oxygen is added at the beginning of the reaction and is rapidly consumed. About 20% oxygen on beechwood is required (16). Other types of wood require different amounts of oxygen.

Higher temperatures lead to faster delignification rates. Temperatures above 150°C (302°F) are suitable to produce a pulp with a brightness above 30% and a yield of less than 60% in about 60 minutes. A temperature of 160°C (320°F) is used in these calculations since that is the temperature of the pulp leaving the refiners. When the same temperature is used in both stages there is no loss of energy between stages.

Cooking chemicals are either sodium hydroxide or sodium carbonate. The use of sodium carbonate in the oxygen stage as active alkali results in pulp of higher brightness, a higher breaking length, and a lower tear factor at the same yields than pulps made with sodium hydroxide as the active alkali (32). The use of sodium carbonate as active alkali also eliminates the need for the energy intensive causticizing plant. 2% Na_2CO_3 on wood was used for calculation purposes.

Oxygen consumption will be greater than 350 Kg/KKg (700 lb/T) pulp produced. High oxygen pressures are used to maintain an excess of oxygen in the reactor liquors. Easily available oxygen in the digestor speeds the lignin destruction leaving less time for the slower cellulose depolymerization reactions to degrade the pulp strength.

Bleaching to high brightness can be accomplished with a DED sequence. Full countercurrent washing would be used. It would not be possible to reuse bleach plant wash water for washing black liquor from the pulp after the oxygen stage because of the difficulty of separating chlorides from the sodium carbonate. In the Rapson process the sodium carbonate is taken out of the white liquor along with the sodium chloride.

The consistency of the pulp during the oxygen reaction affects the pulping rate due to the quantity of dissolved oxygen in the pulping liquor available for reaction. Low consistencies result in high delignification rates (20). A likely method of achieving low consistencies without having to heat large volumes of white liquor is to have a high recirculation rate of black liquor with reoxygenation of the liquor while outside the digestor. This high recirculation rate would cause an increase in oxygen consumption due to further attack of the dissolved wood solids in the liquor (23). Fresh white

liquor would be slowly added, the bleed off going to the pulp wash. Figure 5 shows the process.

Products

The pulps produced by this method are somewhat lower in strength than kraft pulps. The lower strength is due to the mechanical damage to the fibers in the thermomechanical stage. Higher steaming pressures would lead to less fiber damage and thereby stronger pulps. If the thermomechanical step can be optimized and problems of chemical damage of the fiber resolved, the pulps should have strengths comparable to kraft pulps and, therefore, have similar uses.

State of Development

Thermomechanical pulping followed by oxygen delignification is still in the laboratory bench scale stage. Much work is required on process optimization, especially on the thermomechanical stage, before a pilot plant can be built.

The advantage of thermomechanical pulping followed by oxygen delignification over other oxygen pulping methods is that wood residues from other forest products can be used. Chip uniformity or thin chips are not required.

AIR EMISSIONS

Reduced Sulfur Compounds

Although small amounts of sulfur compounds may be present in the cooking liquor, reduced sulfur emissions should not occur from a thermomechanical-oxygen pulping mill. Sulfur compounds will be reduced in the recovery furnace. Since no lime kiln is needed, there are no lime kiln emissions. Oxygen in the pulping stage will immediately oxidize all reduced sulfur compounds. Little reversion of oxidized compounds should occur during black liquor evaporation.

Sulfur Dioxide

Sulfur dioxide emissions should not occur from the recovery furnace at a thermomechanical-oxygen pulping mill. The small quantities of SO_2 that form in the recovery furnace react with the fumes and are removed by the electrostatic precipitators as sodium sulfate. Since there is no lime kiln there will be no sulfur discharge from that potential source.

Sulfur dioxide emissions will occur from the power boiler, the quantity emitted depending upon the sulfur content of the fuel and the amount of energy required. Calculation for SO_2 emissions from a thermomechanical-oxygen pulping mill are contained in Appendix B. Emissions are 2.5 Kg/t (5.0 lb/T) SO_2 for oil fired boilers, 3.9 Kg/t (7.8 lb/t) SO_2 for coal fired boilers, or 0.5 Kg/t (1.0 lb/T) SO_2 for waste wood fired boilers.

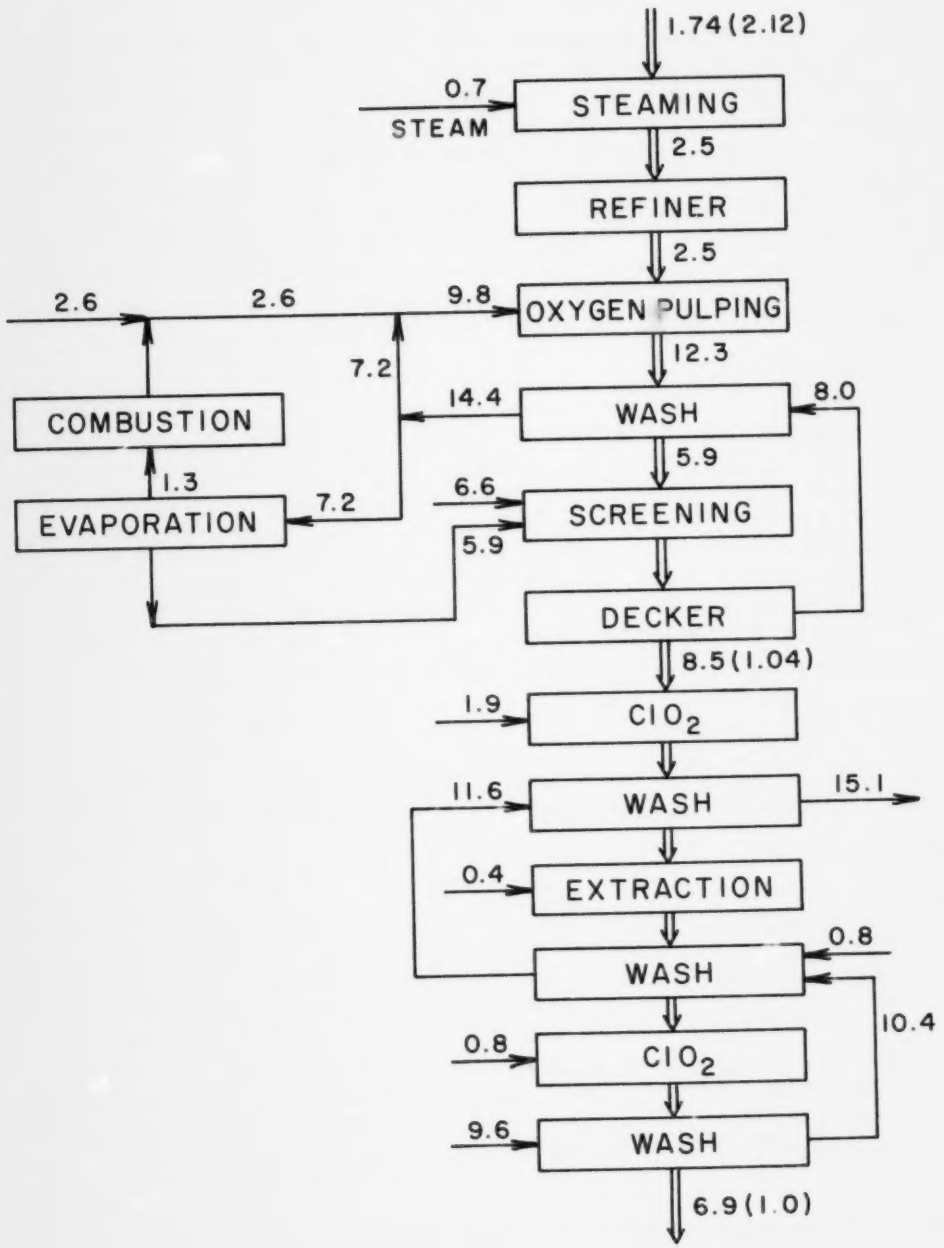

Figure 5. Diagram of a thermomechanical pulping process followed by oxygen delignification

Particulates

Quantities of particulate emissions from oxygen-thermomechanical pulping are listed in Appendix C. Particulates from the recovery furnace should be very low or non-existent due to the low heating value of the black liquor. If supplemental fuel is fired with the black liquor to increase steam production, a higher particulates emission would be expected. Smelt tank particulate emissions are 0.21 Kg/t (0.42 lb/T) pulp. There are no lime kiln emissions since there is no lime kiln. Nearly all of the particulates from an oxygen-thermomechanical mill will result from the power boiler. Particles from a waste wood fired power boiler are estimated to be 0.78 Kg/t (.56 lb/T). The total particulate emissions from an oxygen-thermomechanical mill are estimated to be 1.5 Kg/t (3.0 lb/T) bleached pulp.

Carbon Monoxide

The formation of carbon monoxide in oxygen bleaching mills has been observed. At low consistencies, between 0 and 50 g carbon monoxide/t (0.0-1.0 lb.T) were measured, and at high consistencies (20-30%), 300 to 500 g carbon monoxide/t (0.6-1.0 lb/T) pulp was observed in the degassing line (25). Similar formation of carbon monoxide can be expected in an oxygen pulping system (26). Carbon monoxide formed during oxygen pulping can be handled by venting the pressure relief gases to the recovery furnace or lime kiln air intake, as is done in kraft mills for odor control. There should be no carbon monoxide emissions allowed from an oxygen pulping mill.

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D and are 3.4 Kg/t (6.8 lb/T) for an oxygen-thermomechanical pulp mill.

WATER DISCHARGES

New pulp mills will have the advantage of being able to install the newest technology for control of water effluents. Materials of construction can be chosen so that corrosion is minimized. Old equipment would not require modification or need to be replaced and plant layout can maximize the efficiency of recycle. Water pollution discharges will be lower than existing mills, disregarding the oxygen pulping. Oxygen pulping itself offers several advantages, largely that the chlorination and first extraction stages in the bleach plant are not longer required. Nearly 80% of the bleach plant BOD is contained in the chlorination and first extraction stages of the bleach plant.

A no discharge mill does not appear possible with oxygen-thermomechanical pulp mills. Disposal of the bleach plant waste through the recovery furnace would not be possible as with the Rapson process in a kraft mill. During crystallization of the sodium chloride in the Rapson process sodium carbonate is also precipitated (33). Separation of the carbonate from the chloride by leaching would be extremely difficult.

Biochemical Oxygen Demand

BOD discharge from an oxygen pulp mill is much lower than from a kraft mill. Contributing to the reduced BOD are reuse of decker water on the brown stock wash and elimination of the chlorination and first extraction stage in the bleach plant. Evaporator condensate waters are recycled to the screen and causticizing department. Spills and miscellaneous flows are the only BOD contributions from the pulping area and contain about 3 Kg/t (6.0 lb/T) (43).

Bleach plant effluents will be much less than from kraft mills. The oxygen pulping stage eliminates the need for the chlorine and first stage extraction step. The largest flow will be from the chlorine dioxide stage wash. BOD from the DED bleaching sequence in a kraft mill is between 2 and 3 Kg/t (4-6 lb/T) pulp (33), (34). Raw BOD loadings from an oxygen mill bleach plant will be slightly higher than a kraft mill DED portion of the bleach plant because of carry over of black liquor solids from the decker into the bleach plant. BOD loading from an oxygen bleach plant should be about 3 to 4 Kg/t (608 lb/T) pulp.

Total BOD raw waste loading from an oxygen pulp mill is about 6 to 7 Kg/t (12-14 lb/T) pulp. Assuming a 90% efficient waste treatment system, final BOD discharges will be in the range of .6 to .7 Kg/t (1.2-1.4 lb/T).

Suspended Solids

Because of the reduced discharges due to recovery of decker effluents and shortened bleaching sequences, suspended solids discharges will be much reduced. Suspended solids would enter the sewer through spills, water treatment plant sludges, and bleach plant effluents. Spills will contribute about 5 Kg/t (10 lb/T) suspended solids.

Most of the suspended solids in the raw waste load will be removed by primary and secondary treatment. Solids produced by biological activity during secondary treatment will make up the bulk of suspended solids in the effluent and are directly related to the BOD and the method of treatment. Assuming a concentration of 100 mg/l suspended solids escaping in the effluent and a flow of 28,000 l/t (6717 gal/T) pulp, suspended solids leaving with the treated effluent are 2.8 Kg/t (5.6 lb/T) pulp.

Color

Oxygen pulping liquors have about one fourth the color of kraft or soda liquors (12), (29). Spills from screening and deckers would thereby contain relatively little color. The strongly colored chlorine extraction stage effluent would also not be present. Color would be much less than found in kraft mill effluents.

Toxicity

Conditions present during oxygen pulping destroy resin and fatty acids that are responsible for toxicity in many pulp mill discharges (30). Other toxic materials, such as methyl mercaptan and methyl sulfide, are not present

because of the absence of reduced sulfur. Bio-assay tests have shown that oxygen pulping liquors are non-toxic (12). Chlorination stage bleach plant effluents, which contribute a large amount of toxicity to kraft mill effluents, are not present in oxygen pulping mills. Chlorine dioxide bleaching effluents have been shown to be less toxic than chlorination stage effluents (5).

SOLID WASTES

Solid wastes from an oxygen-thermomechanical mill derive from several sources: process losses including wood preparation, green liquor dregs, washing and screening losses, bleach plant wastes, drying wastes, and spills; water treatment sludges; fly ash; and biological solids developed from treatment of effluents.

Process solids losses can be estimated by assuming that 90% of the suspended solids in the effluent are removed in the primary and secondary clarifier. Process solids losses are estimated to be 8 Kg/t (16 lb/T) and process solids to be disposed of to be 7.2 Kg/t (14.4 lb/T).

Water treatment waste solids are dependent upon the quality and quantity of the water to be treated. Water quality is highly variable depending upon location and season and thereby making estimates of sludges produced difficult. Water use in an oxygen-thermomechanical mill would be less than that of kraft so the solids produced by this source are less.

Fly ash generation will depend upon the quantity of energy required and the type of fuel used in the boiler. Bark and coal will produce the greatest quantity of fly ash, whereas gas or oil will produce none. Use of external energy is greater for oxygen-thermomechanical pulping so fly ash generation will be greater.

Biological solids derived from secondary treatment of effluents are the largest solids waste disposal problem. They have a high volume to dry weight ratio when wet and are difficult to dewater. The quantity of biological solids produced depends upon the quantity and quality of the effluent and the detention time of the secondary treatment. Activated sludge systems will produce more solids than will an aerated lagoon. Overall, an oxygen-soda mill will produce less biological solids than a kraft mill because of the lower raw BOD loading to the treatment plant.

ENERGY

The major energy using operations in an oxygen-thermomechanical mill are pulping, evaporation, bleaching, and oxygen production. Oxygen-thermomechanical pulping differs in energy usage from typical kraft mills in several aspects. Since sodium bicarbonate is used as the active alkali, there is no need to causticize the green liquor, resulting in considerable energy savings. The oxidation of organics in the oxygen stage results in less energy produced by the recovery furnace, but the energy produced by the oxidation reactions helps heat the digestor. There is enough heat produced in the reactor by lignin oxidation to make the pulping stage a net exporter of energy. Although

the wood processing takes place in two reactor steps there is no energy loss. All of the heat applied in the precooking and refining stage is transferred to the oxygen stage. Oxygen-thermomechanical pulping requires a short bleach sequence resulting in an additional energy savings. The production of high pressure pure oxygen requires a considerable amount of energy.

The total energy required from external sources to an oxygen-thermomechanical mill is 617 KKcal/t (2221 KBTU/T) bleached pulp. All of the external energy requirements will be for electrical power. Some excess power boiler capacity may be required for electricity production, with process steam being available in excess.

SECTION 9

OXYGEN PULPING OF CHIPS

PROCESS DESCRIPTION

Wood is cut into shavings or wafers parallel to grain to a thickness of 1 mm. The chips are cooked at 130°C for 16 hours with oxygen and 20 to 22% sodium carbonate on wood. The carbonate is added as the cook progresses and carbon dioxide is relieved several times during the cook to maintain a pH of 8.0. High pH's are avoided (34). Screen rejects are 3.6%, giving a yield of 54% (35). Yields can be increased by lower cooking temperatures and shorter times. Carbohydrate stabilizers (30 g/l KI) are added to improve pulp quality and yield.

The pulp is washed and screened. The liquors are evaporated and incinerated or wet oxidized for recovery of chemicals. If KI is used in the process, wet oxidation is a likely chemical recovery means because of the high volatility of KI (24). No causticizing plant is required. The pulp can be bleached in a DED sequence. Figure 6 shows the process.

Products

Oxygen pulps that use potassium iodide in the cook as a carbohydrate inhibitor have breaking lengths equal to that of kraft, superior burst factors, but lower tear factors than kraft pulps. The pulp would be good for producing liner board, bag, and construction paper.

State of Development

Oxygen pulping of chips is still in the bench scale stage. The process should be ready for a pilot scale trial.

AIR EMISSIONS

Reduced Sulfur Compounds

Although small amounts of sulfur compounds may be present in the cooking liquor, reduced sulfur emissions should not occur from an oxygen chip pulping mill. Sulfur compounds will be reduced in the recovery furnace. Since no lime kiln is needed, there are no lime kiln emissions. Oxygen in the pulping stage will immediately oxidize all reduced sulfur compounds. Little reversion of oxidized compounds should occur during black liquor evaporation. There should be little sulfur in the system because the only source of sulfur is raw water makeup and chemical impurities.

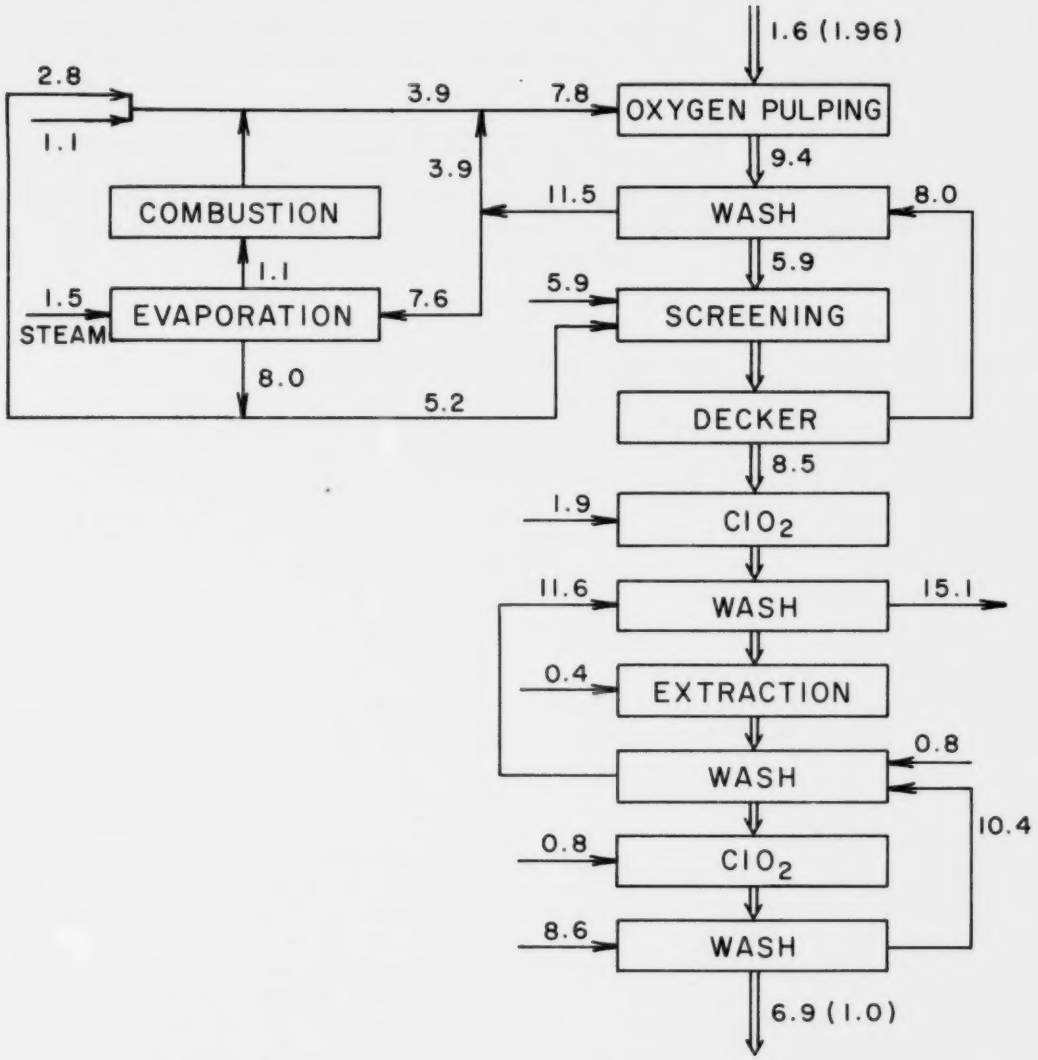

Figure 6. Diagram of oxygen pulping of chips process

Sulfur Dioxide

Sulfur dioxide emissions should not occur from the recovery boiler at an oxygen chip pulping mill. The small quantities of SO_2 that form in the recovery furnace react with the fumes and are removed by the electrostatic precipitators as sodium sulfate. Since there is no lime kiln, there will be no sulfur discharge from that potential source.

Sulfur dioxide emissions will occur from the power boiler, the quantity emitted depending upon the sulfur content of the fuel and the amount of energy required. As shown in Appendix B, SO_2 emissions from the power boiler at an oxygen chip pulping mill are 3.2 Kg/t (6.4 lb/T) pulp for oil fired boilers, 5.0 Kg/t (10.0 lb/T) pulp for wood waste fired boilers.

Particulates

Particulate emissions are shown in Appendix C. Particulate emissions from an oxygen chip pulp mill total 4.8 Kg/t (9.6 lb/T) pulp. Particulate emissions from the recovery furnace are low--0.59 Kg/t (1.18 lb/T) pulp because of the low heating value of the black liquor. Smelt tank emissions are 0.23 Kg/t (0.46 lb/T) pulp. The lack of a lime kiln precludes lime kiln emissions. Power boiler emissions of 1.3 Kg/t (2.6 lb/T) pulp from a waste wood fired boiler make up the bulk of the emissions. Total particulate emissions from an oxygen chip pulping mill is estimated to be 2.12 Kg/t (4.24 lb/T).

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D and are estimated to be 3.4 Kg/t (6.8 lb/T) for an oxygen chip pulping mill.

Iodide

If iodide is used as a cellulose degradation inhibitor in the oxygen delignification stage, there is a possibility of iodide emissions from the recovery furnace. At the normal recovery furnace bed surface temperature of 928°C (1800°F), sodium iodide has a vapor pressure of 28 mm Hg. At this high vapor pressure considerable amounts of sodium iodide will be vaporized. Sodium chloride, which has a vapor pressure lower than sodium iodide is known to varporize from kraft mill recovery furnaces. Condensation of the iodide will form a fume. The fumes can probably be removed from the flue gas via an electrostatic precipitator with other particulates. Electrostatic precipitators do a poor job of removing sodium chloride, so they may do a poor job of removing sodium iodide.

About 60 Kg NaI/t (120 lb NaI/T) pulp is projected. Assuming 98% efficiency for the brown stock washers, and about 40% of the NaI in the black liquor being vaporized, of which 50% will be captured in the direct contact evaporator and 98% of the remainder removed by the electrostatic precipitator, NaI emissions would be about 0.24 Kg/t pulp.

Carbon Monoxide

The formation of carbon monoxide in oxygen bleaching mills has been observed. At low consistencies, between 0 to 50 g carbon monoxide per ton (0-0.1 lb/T) were measured, and at high consistencies (20-30%), 300 to 500 g carbon monoxide per ton (0.6-1.0 lb/T) were observed in the degassing line (30). Similar formation of carbon monoxide can be expected in an oxygen pulping system. Carbon monoxide formed during oxygen pulping can be handled by venting the pressure relief gases to the recovery furnace or lime kiln air intake as is done in kraft mills for odor control. There should be no carbon monoxide emissions allowed from an oxygen pulping mill.

WATER DISCHARGES

New pulp mills will have the advantage of being able to install the newest technology for control of water effluents. Materials of construction can be chosen so that corrosion is minimized. Old equipment would not require modification or need to be replaced, and plant layout can maximize the efficiency of recycle. Water pollution discharges will be lower than existing mills disregarding the oxygen pulping. Oxygen pulping itself offers several advantages, largely that the chlorination and first extraction stages in the bleach plant are no longer required. Nearly 80% of the bleach plant BOD is contained in the chlorination and first extraction stages of the bleach plant.

A zero discharge mill does not appear possible with oxygen chip pulp mills. Disposal of the bleach plant waste through the recovery furnace would not be possible as with the Rapson process in a kraft mill. During crystallization of the sodium chloride in the Rapson process, sodium carbonate is also precipitated (33). Separation of the carbonate from the chloride by leaching would be extremely difficult.

Biochemical Oxygen Demand

BOD discharges from an oxygen pulp mill are much lower than from a kraft mill. Contributing to reduced BOD are reuse of decker water on the brown stock wash and elimination of the chlorination and first extraction stage in the bleach plant. The evaporator condensate waters are recycled to the screen and causticizing department. Only pollutants from the pulping stage would be from leaks and spills. Spills and miscellaneous flows amount to about 3 Kg/t (6 lb/T) (15).

Bleach plant effluents will be much less than compared to kraft mill bleach plants. The oxygen pulping stage eliminates the need for the chlorine and first extraction step. The largest flow will be from the chlorine dioxide stage wash. BOD from the DED bleaching sequence in a kraft mill is between 2 and 3 Kg/t (4-6 lb/T) pulp (27), (28). Raw BOD loadings from an oxygen mill bleach plant will be slightly higher than a kraft mill DED portion of the bleach plant because of carry over of black liquor solids from the decker into the bleach plant. BOD loading from an oxygen bleach plant should be about 3 to 4 Kg/t (6-8 lb/T) pulp.

Total BOD raw waste loading from an oxygen pulp mill is about 6 to 7 Kg/t (12-14 lb/T) pulp. Assuming a 90% efficient waste treatment system, final BOD discharges will be in the range of .86 to .96 (kg/t (1.72-1.92 lb/T).

Suspended Solids

Because of the reduced discharges due to recovery of decker effluents and short bleaching sequences, suspended solids discharges will be much reduced. Suspended solids would enter the sewer through spills, water treatment plant sludges, and bleach plant effluents. Spills will contribute about 5 Kg/t (10 lb/T) suspended solids, and boiler room effluents will contribute about 1 Kg/t (2 lb/T) suspended solids.

Most of the suspended solids in the raw waste load will be removed by primary and secondary treatment. Solids produced by biological activity during secondary treatment will make up the bulk of suspended solids in the effluent and are directly related to the BOD removed and the method of treatment. Assuming a concentration of 100 mg/l suspended solids escaping in the effluent and a flow of 28,000 l/t (6717 gal/T) pulp, suspended solids leaving with the treated effluent are 2.8 Kg/t (5.6 lb/T) pulp.

Color

Oxygen pulping liquors have about one fourth the color of kraft or soda liquors (12), (29). Spills from screening and deckers would thereby contain relatively little color. The strongly colored chlorine extraction stage effluent would also not be present. Color would be much less than that in the effluent from a kraft mill.

Toxicity

Conditions present during oxygen pulping destroy resin and fatty acids that are responsible for toxicity in many pulp mill discharges (30). Other toxic materials such as methyl mercaptan and methyl sulfides are not present because of the absence of reduced sulfur. Bio-assay tests have shown that oxygen pulping liquors are non-toxic (12). Chlorination stage bleach plant effluents, which contribute a large amount of toxicity to kraft mill effluents, are not present in oxygen pulping mills. Chlorine dioxide bleaching effluents have been shown to be much less non-toxic than chlorination stage effluents (5).

SOLID WASTES

Solid wastes from an oxygen pulping mill derive from 4 main sources: 1) process losses; including wood preparation, green liquor dregs, washing and screening losses, bleach plant wastes, drying wastes, and spills; 2) water treatment sludges; 3) fly ash; and, 4) biological solids developed from treatment of effluents.

Process solids losses can be estimated by assuming that 90% of the suspended solids in the effluent are removed in the primary clarifier. Knots

and shives are re-refined. Process solids losses are estimated to be 6 Kg/t (12 lb/T), and process solids to be disposed of to be 5.4 Kg/t (10.8 lb/T).

Water treatment waste solids are dependent upon the quality and quantity of the water to be treated/ Water quality is highly variable, depending upon location and season, thereby making estimates of sludges produced difficult. Water use in an oxygen pulping mill would be less than that of kraft, so the solids produced by this source are less.

Fly ash generation will depend upon the quantity of energy required and the type of fuel used in the boiler. Bark and coal will produce the greatest quantity of fly ash, whereas gas or oil will produce none. Use of external energy is much greater for oxygen pulping, so fly ash generation will be much greater.

Biological solids derived from secondary treatment of effluents are the largest solids waste disposal problem. They have a high volume to dry weight ratio when wet and are difficult to dewater. The quantity of biological solids produced depends upon the quantity and quality of the effluent and the detention time of the secondary treatment. Activated sludge systems will produce more solids than will an aerated lagoon. Overall, an oxygen pulping mill will produce less biological solids than a kraft mill because of the lower raw BOD loading to the treatment plant.

ENERGY

The major energy uses in an oxygen pulp mill are evaporation of black liquor, oxygen manufacture, and bleaching. Digestor heating would normally require a large amount of energy, but the oxidation reaction within the digestor should be able to provide more than the required amount. Oxidation of organics in the digestor leaves less organics to be burned in the recovery furnace. The energy produced by the recovery furnace is considerably less than found in kraft mills. The higher yield of oxygen pulping also decreases the amount of energy produced in the recovery furnace. The manufacture of high pressure oxygen requires 1820 KKcal/t (6553 KBTU/T) O_2. At 20% oxygen on wood, oxygen manufacture is a major energy consumer. Oxygen pulps are easily bleached, thus requiring short bleaching sequences and thereby resulting in some energy savings over a kraft bleach sequence. No energy is used in causticizing green liquor because sodium carbonate is used as the active alkali in the digestor.

Oxygen pulping will require additional power production facilities to produce 951 KKcal/t (3424 KBTU/T) pulp. Power boilers for electricity production would be the most likely additional energy source.

SECTION 10

CHLORIDE DIOXIDE PULPING

PROCESS DESCRIPTION

Pulping with halogens has long been considered as a pulping process because of the high selectivity of chlorine compounds in their attack on lignin while leaving the cellulose compounds intact. The major obstacle to halogen pulping has been its cost. New interest has developed for halogen pulping because of its pollution free potential. Energy use remains a prime consideration.

Of the halogen compounds, ClO_2 is one of the faster acting and more selective compounds available. Chlorine dioxide pulping processes that have been investigated are of two types: pulping of chips, and delignification of thermomechanical pulp. Pulping of chips has the problem of uneven pulping. The action of chlorine dioxide on the chips is very rapid. The reaction on the exterior of the chip is complete before the chlorine dioxide can diffuse to the interior of the chip, resulting in high chemical usage. Several investigations have been made concerning chlorine dioxide pulping of thin chips to reduce the above problems (36), (37).

When thermomechanical pulp is delignified by ClO_2, the lignin coating the separated fibers is readily available to attack by the ClO_2. Only enough ClO_2 is used to render the lignin soluble, resulting in substantial savings in chemical costs.

Thermomechanical Stage

When preparing the thermomechanical pulp, care must be taken so as not to damage the individual fibers during refining. The significant process variables in the thermomechanical stage are the cook time, cook temperature, and refiner rpm and clearance. Sufficient time in the preheater is required to raise the chips to a uniform temperature. Less than 5 minutes are required for heating the chips. The preheating temperature governs the amount of lignin softening that occurs.

When wood chips are heated, the lignin and hemicelluloses between the cell walls becomes soft. The softening of the lignin begins at specific temperatures referred to as the glass point. The glass point for each species of wood is different. During cooking the lignin is heated to the glass point so that fibers can be easily separated upon refining. At temperatures below the glass point the wood fractures through the outer layer of the secondary cell wall. At temperatures above the glass point the wood fractures through the lignin layers between the cells. When wood has been fiberated above the

glass point, the fibers will be coated with a layer of lignin. The transition between refined spruce fracturing in the cell wall or fracturing between the cell wall occurs between 120°C (248°F) and 135°C (275°F) (31). The thermomechanical pulps will be stronger if the fibers have not been torn. A thermomechanical stage temperature of 160°C (320°F) was used in the calculations for this paper.

Lignin modification with about 8% ClO_2, or with a mixture of 77% ClO_2 and 38% Cl_2, takes place at 60°C for about 60 minutes in the chlorine dioxide delignification reactor. Lignin is separated from the pulp with 7.5% sodium hydroxide in an extraction step. Pulp yield is 59%. The pulp is then ready for bleaching to a TAPPI brightness of 85 with a D/CED sequence (28), (39), (40).

Pulping chemicals can be recovered by evaporation and burning the pulping liquor. A mixture of sodium chloride and sodium carbonate are produced. The smelt is causticized and the NaOH and NaCl separated by crystallization. Chlorine, hydrogen, sodium hydroxide, and sodium chlorate are produced by electrolysis of the sodium chloride. Chlorine dioxide is produced with HCl, from burning of H_2 and Cl_2, and sodium chlorate (36).

There is no effluent from halo pulping as evaporator condensates can be used for washing of the final bleached pulp. Bleach plant effluents are recycled through the screening room to the brown stock washers so that bleaching chemicals are recovered. Since there is no chlorine stage in the bleach plant, bleach plat water use will be low. The process is diagrammed in Figure 7.

Products

Chlorine dioxide pulping produces a very strong bleached pulp but has poor tear properties. Semibleached pulps are possible. Pulp can be sold in direct competion with bleached kraft market pulp where tear is not a critical property. Paper products would include specialty papers, tissue and toweling, wrapping papers, bags, towels, linerboard, boxboard, and newsprint stock.

State of Development

Chlorine dioxide pulping is in different stages of development in different parts of the world. In the United States the process is at the bench scale level (38), (39). In Japan a 10 ton per day pilot plant has been built (36), (41).

AIR EMISSIONS

Reduced Sulfur Compounds

Reduced sulfur compounds should be non-existent in a chlorine dioxide pulping mill. Sulfur in any form should not exist in the process. Small amounts of sulfur that enter the process as contaminants should be purged or removed.

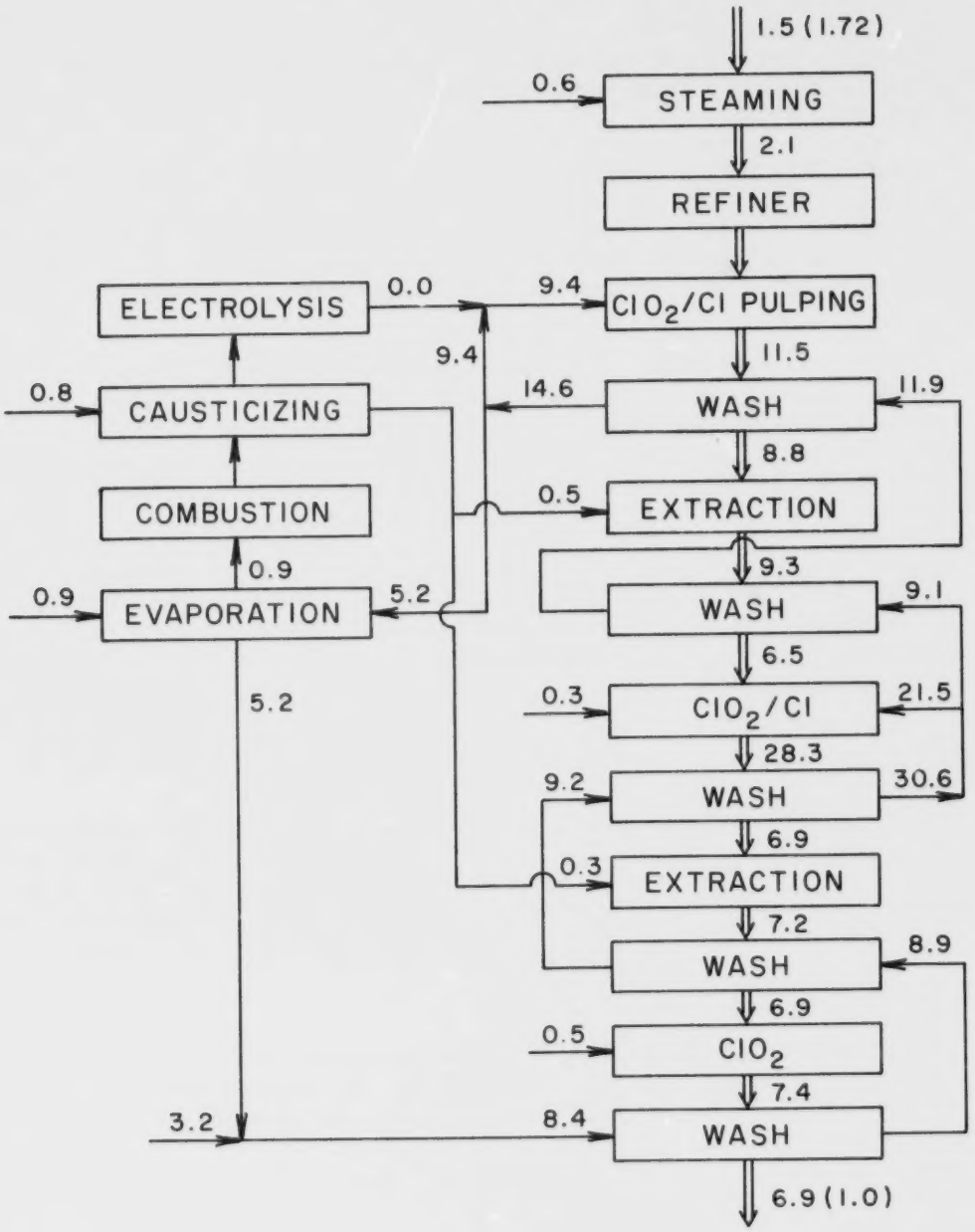

Figure 7. Diagram of a ClO_2 pulping process

Sulfur Dioxide

As there are no sulfur compounds in the pulping chemicals, there should be no sulfur dioxide emissions from the recovery furnace. Small quantities of SO_2 may be emitted from the lime kiln due to sulfur in the fuel oil. Sulfur dioxide will also be emitted from the power boiler at a rate of 0.8 Kg/t (1.6 lb/T), according to Appendix B.

Particulates

Particulate emissions from various sources are listed in Appendix C. Nearly all of the particulate emissions from a halogen pulping mill are chlorides from the recovery furnace. Two factors cause the high particulate emissions: a high rate of fume formation in the recovery furnace, and a reduced electrostatic precipitator collection efficiency for sodium chloride. Fume formation in the recovery furnace will be accelerated because of the high heating value of the black liquor and the high concentration of sodium chloride in the black liquor. The high heating value will result in a high temperature in the furnace. The high furnace temperature will increase the volatilization of sodium chloride. Sodium chloride boils at a much lower temperature than do other pulping chemicals. About 60% of the chloride may be vaporized resulting in 121 Kg/t (242 lb/T) pulp fumes. About 50% will be adsorbed in the direct contact evaporators leaving about 60 Kg/t (120 lb/T) to the electrostatic precipitator.

Collection efficiencies of electrostatic precipitators for NaCl are less than for salt cake (42). Salt fumes fail to agglomerate and will pass through the electrostatic precipitator (43). Furthermore, the volume of gas to be treated in a ClO_2 pulp mill will be greater than that for a kraft mill. Assuming an electrostatic precipitator with an efficiency of 98%, particulate emissions from a chlorine dioxide pulping mill would be about 1.2 Kg/t (2.4 lb/T) pulp. Emissions are lower than might be expected because of the smaller quantity of non-organic solids per ton pulp that are fired in the recovery furnace.

Particulate emissions from other sources are listed in Appendix C. Total particulates from a chlorine dioxide mill are approximately 2.6 Kg/t (5.2 lb/T) bleached pulp.

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D and are estimated to be 8.9 Kg/t (17.8 lb/T) for a chlorine dioxide pulping mill.

WATER DISCHARGES

The chlorine dioxide pulping process recovers all of the process streams for pulping chemical and energy production. Flows from the mill would consist of spills and wash downs. Assuming that a modern mill would be constructed with sufficient storage capacity to collect spills, there should be very little discharge from a chlorine dioxide pulping process. Those flows resulting from washup could be evaporated in the process. A small amount of in-

organic blowdown would be required to prevent the buildup of impurities in the system.

SOLID WASTES

Solid wastes from chlorine dioxide pulping mills will derive from wood preparation, green liquor dregs, drying wastes, spills, and fly ash. The solid wastes will consist of primarily inorganic material and will, thereby, be fairly easy to dispose of.

Wood preparation solids wastes will consist mainly of sand, grit, and bark fines from washing of logs, or of sand and clays from washing of chips. Green liquor dregs may be difficult to dispose of by themselves because they are quite hydrous and difficult to thicken (44).

Since chlorine dioxide pulping has no effluent, there will be no biological solids produced. Reuse of most internal water streams will greatly reduce the need for water treatment, and thereby greatly reduce the quantity of water treatment solids to be disposed of. Overall, the chlorine dioxide pulping processes will have little solids to dispose of.

ENERGY

The major detriment to the commercialization of chlorine dioxide pulping has been the energy required for production of the pulping chemicals. Of all the pulping alternatives considered in this paper chlorine dioxide pulping will require the most auxilliary power production. Examination of Table 17 will show that the chlorine dioxide pulping process, including production of chlorine chemicals, requires 107 KKcal/t (385 KBTU/T) pulp more purchased fuel heat value than does kraft pulping. The large energy requirement for chlorine dioxide production is largely offset by energy savings due to less causticizing capacity, lower digestor temperatures and the shorter bleaching sequence. The real reason that chlorine dioxide pulping has an overall high energy requirement is the high yield of 58%. The high yield results in less organics to be burned in the recovery furnace and thus in less internal energy production. A decrease in the overall yield to 50% would provide an extra 850 KKcal/t (3060 KBTU/T) pulp, making chlorine dioxide pulping energy requirements compare favorably with the other pulping sequences. In an actual mill, the yield will probably be kept high because of the high value of wood and because of the loss of pulp strength observed at the lower yields.

The chlorine dioxide pulping process requires 1456 KKcal/t (5242 KBTU/T) pulp purchased energy of which 1237 KKcal/t (4454 KBTU/T) is from power boilers.

SECTION 11

SOLVENT PULPING

PROCESS DESCRIPTION

Solvent pulping uses low molecular weight organic compounds to dissolve lignin from wood chips and thereby affect fiberization. Solvents that have been investigated for use in solvent pulping are ethanol, butanol, methyl ethyl ketone, acetone, and cyclohexanone (45), (46). These solvents can be recovered and produced on site. Ammonia can be added to the solvent to aid in dissolving the lignin.

Chips enter the digestor from the top where the temperature is 180 to 210°C (356 to 410°F). The high temperatures necessitate high pressure equipment. The chips move through the digestor counter currently to the solvent. Fresh solvent entering at the low end of the digestor serves as a wash for the pulp. The used solvent leaves the top of the digestor, and is flashed into a rectifying column, where the solvent is separated from the organics and water that was in the wood. The solvent is condensed, heated and returned to the digestor. The lignin separates from the water phase as a thick viscous liquid, and can be dried to a powder. Hydrogenation of the powder produces alcohols and ketones. The pulp is washed and bleached. The optimum bleaching sequence has not been determined.

Products

Pulp produced by solvent pulping has strengths ranging from those similar to sulfite to those similar to kraft, depending upon the solvent used. The higher strength solvent pulps have lower tear than kraft because of the higher hemicellulose content of the solvent pulps. The pulps could be used in place of kraft pulps except where high tear strength is required.

State of Development

Solvent pulping is still in the laboratory stage of development. Because of its early stage of development it is difficult to determine what its effluent and emission characteristics will be.

AIR EMISSIONS

Reduced Sulfur Compounds

As there are no sulfur containing chemicals in a solvent pulping mill there will be no reduced sulfur emissions.

Sulfur Dioxide

Since there are no sulfur containing chemicals used in a solvent pulping mill there will be no sulfur dioxide emissions from the process. Sulfur dioxide emissions can be expected from the power plant if sulfur containing fuels are used. The amount of sulfur dioxide emissions from a solvent pulping mill will be determined by the energy requirements of the process. The process is not at a stage of development where the energy requirements can be determined.

Particulates

The black liquor will contain no inorganic materials; when fired in the recovery furnace there will be no formation of difficult to remove inorganic fumes. Pyrolysis solids can be expected to be carried out of the recovery furnace, but these are easily removed.

Some particulates may be expected from power boilers if coal or hog fuel is used. The quantity of this material will depend upon the fuel used and the energy required by the mill.

Organic Vapors

The use of volatile organic pulping liquor could lead to the escape of organic vapors to the atmosphere. All pulping and washing operations would need to be totally enclosed. Prevention of vapor leaks at the chip high pressure feeder would be difficult. Scrubbing of organic vapors with water sprays should remove organic fumes because of their high solubility in water.

WATER DISCHARGES

Discharges from a solvent pulping mill could consist of wash water and bleach plant effluents. The brown stock wash water will require stripping to remove residual volatile organic pulping liquors. Lignin materials dissolved during pulping of the pulp are washed first with solvent to remove soluble wood materials. Bleach plant effluents should be about the same as those expected from the kraft pulping process.

Biological Oxygen Demand

Raw BOD from the bleach plant will be about 10-15 Kg/t (20-30 lb/T). There should be no decker wash water since this water should be totally collected for solvent recovery. After secondary treatment, the BOD in the effluent would be 1 Kg/t (2 lb/T) pulp.

Total Suspended Solids

Suspended solids in the raw effluent should be removed by primary and secondary treatment. Solids in the effluent would be comprised largely of biological solids produced during secondary treatment. Suspended solids in the effluent should be less than 2 Kg/t (4 lb/T), depending upon the type of secondary treatment and the effluent flow. The 2 Kg/t (4 lb/T) number was arrived at by assuming flows and BOD strengths from the solvent process

to be similar to those from the kraft or soda process.

Toxicity

The toxicity of the effluents from a solvent pulping mill are difficult to assess because of lack of information. Toxicity due to the bleach plant would still be present. Resin acids probably will not be a problem in a solvent pulping mill. There will be no turpentine separation or relief gas condensates. In summation, toxicity of the effluent from a solvent pulping mill should be less than that from a kraft mill.

Color

Color will be present from the bleach plant chlorine extraction stage. Decker color will not be present. The color in the effluent from a solvent pulping mill should be less than from a kraft mill.

SOLID WASTES

Solid wastes from a solvent pulping mill will derive from 4 main sources: 1) process lossess including wood preparation, washing and screening losses, bleach plant wastes, drying wastes, and spills; 2) water treatment sludge; 3) fly ash; and 4) biological solids developed from treatment of effluents.

Process losses are estimated by assuming they are 90% of the raw waste load suspended solids, that which would be removed in the primary clarifier. Process solids losses are estimated at 11 Kg/t (22 lb/T) pulp. Water treatment sludges will depend upon the quantity and quality required for the process. There is no substantial difference in water requirements between kraft and solvent pulping. The large water usage area, bleaching, is common to both processes.

Biological solids derived from secondary treatment of effluents are the largest solid waste disposal problem. They have high volume to dry weight ratio when wet, and are difficult to dewater. The quantity of biological solids produced depends upon the quantity and quality of the effluent and the detention time of the secondary treatment. Activated sludge systems will produce more solids than will an aerated lagoon. Because of the slightly lower BOD from a solvent pulping mill as compared to a kraft mill, biological solids production will be less.

ENERGY

There is insufficient process information to make energy use calculations for the solvent pulping process.

It may be possible for a solvent pulping mill to be nearly energy self sufficient. The black liquors will not contain inorganic materials which serve to reduce energy recovery in the recovery furnace. Also, the weak black liquor will contain mostly organics, which have lower heats of evaporation than does water. Major energy consumers will be heating the large volumes of cooking liquors to high temperatures and production of hydrogen for hydrogenation of dried lignin to produce pulping chemicals.

SECTION 12

RAPSON PROCESS

PROCESS DESCRIPTION

The Rapson process was developed to remove chlorides from the kraft recovery system specifically so that bleach plant effluents could be disposed of by incineration in the recovery boiler. Bleach plant effluents are to be added to the chemical recovery cycle at the appropriate locations, specifically to the screening room, brown stock washers, green liquor dissolving tank, and lime mud washing. Chlorides are to be removed by crystallization from concentrated white liquor, thus maintaining a sodium chloride concentration in the white liquor of 30 g/l. Evaporator condensate will be stripped and returned to the bleach plant as wash and makeup water. Extensive water reuse in the bleach plant will be required to keep water volumes low. The Rapson process has no effluent. Figure 8 shows the process.

Products

The Rapson process is a modification of the kraft process. The same products would be produced by the Rapson process as would be produced by the kraft process.

State of Development

Parts of the process have been developed through pilot plant work. A full scale mill is being constructed by Great Lakes Paper Co. in Ontario, Canada.

AIR EMISSIONS

Reduced Sulfur Compounds

No difference in reduced sulfur emissions are expected between the Rapson process and a normal kraft process. Kraft pulp mills located near the coast which use salt water transported logs and have high sodium chloride; levels in their cooking liquor have about the same total reduced sulfur emissions from the recovery boiler as do kraft mills which do not contain salt in their cooking liquors (47). When bleach plant effluents are used as brown stock wash water, care will need to be taken to be sure that the wash water is alkaline. Acidic wash water would cause the release of H_2S from the residual Na_2S in the brown stock. Total reduced sulfur emissions should be 0.25 Kg/t (0.5 lb/T) from the recovery furnace and 0.125 Kg/t (0.25 lb/T) from the pulp washers resulting in a total of 0.375 Kg/t (0.75 lb/T) pulp reduced sulfur emissions from the Rapson pulping process (48).

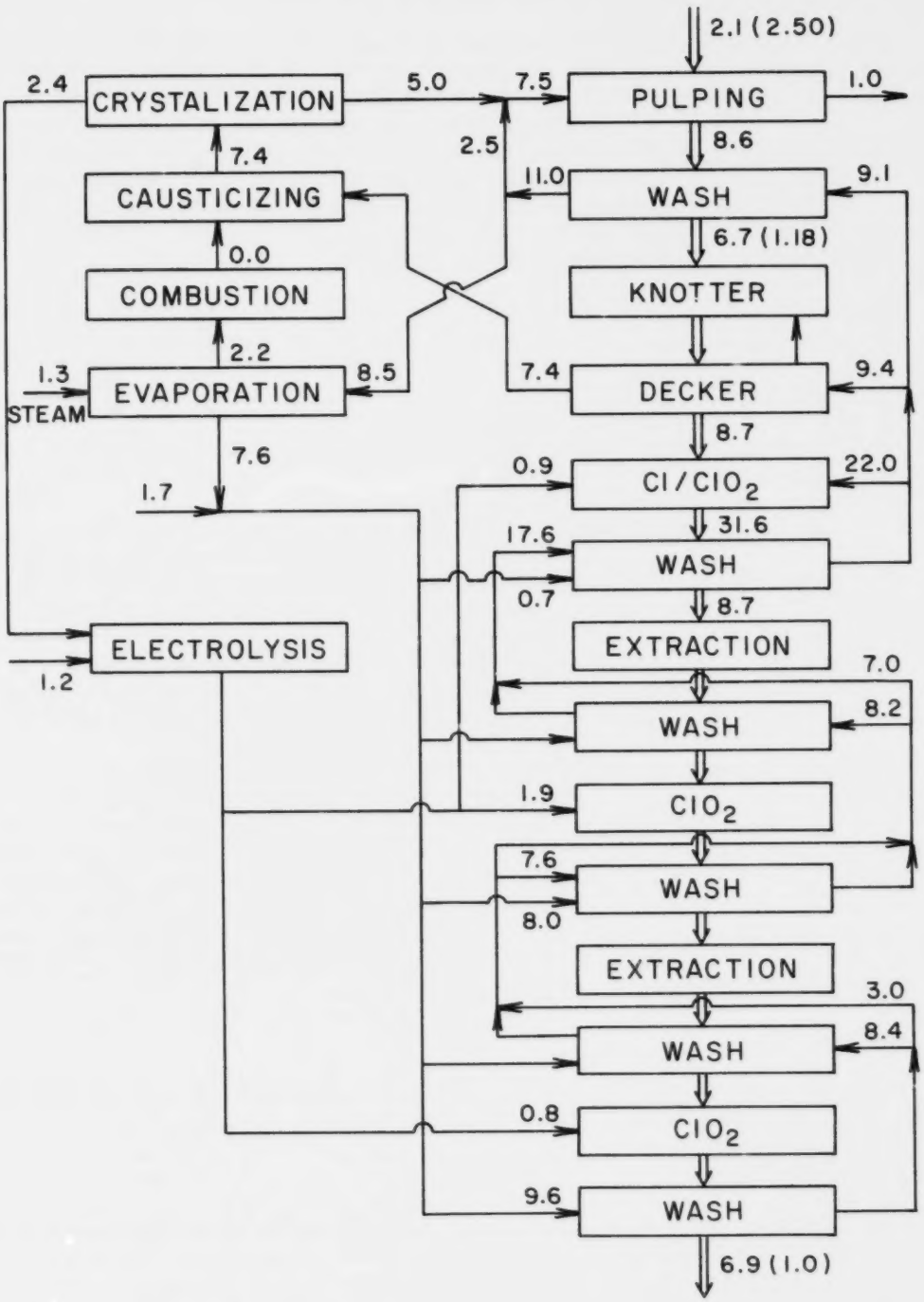

Figure 8. Diagram of the Rapson process

Sulfur Dioxide, Particulates, and Hydrogen Chloride

Sulfur dioxide, particulates, and hydrogen chloride emissions are considered together because they are interrelated. Sulfur dioxide formation at the furnace bed and combustion zone is dependent upon the sulfidity of the black liquor. Higher sulfidities result in greater SO_2 formation. Higher bed temperatures will also cause greater SO_2 formation. Particulate formation is also dependent on the furnace temperature. Higher temperatures result in more sodium vaporization from the furnace bed. Sodium chloride is more volatile than other sodium compounds, so the presence of sodium chloride will increase the quantity of sodium vaporized.

Vaporized sodium then reacts with SO_2 and CO_2 to form sodium sulfate and sodium carbonate fumes (49). The fumes consist of about 90% Na_2CO_3 depending upon the recovery system operation and the sulfidity (3). If the sulfidity is high, the amount of Na_2CO_3 will be small and there will be an excess of SO_2 in the flue gas. In the Rapson process, NaCl will be present in the flue gas. If there is excess SO_2 in the flue gas, the following reaction takes place to form hydrochloric acid (50).

$$SO_2 + 2NaCl + O_2 + H_2O \quad Na_2SO_4 + 2HCl$$

Two Swedish mills, with white liquor salt contents of 10 and 17 Kg NaCl/ton solids in the black liquor and sulfidities of 37% and 35%, reported 200 and 350 ppm HCl in their flue gas, respectively (50). Figure 9 shows the percent HCl of the total chloride in the flue gas as a function of sulfidity (50). It should be noted that most U.S. mills do not have the high sulfidities that Swedish mills have, but range between 20% and 30% sulfidity.

The Rapson process can expect to have lower SO_2 emissions and higher particulate and hydrogen chloride emissions from the recovery boiler than kraft mills would have. Assuming a sulfidity of 25%, SO_2 emissions should be around 150 ppm, or 2 Kg SO_2/t pulp (4 lb/T). From Appendix C, particulate emissions from the recovery furnace are 2 Kg/t (4lb/T) pulp. HCl emissions are estimated by assuming 20% of the chloride fired to the furnace being vaporized, 25% of the vaporized chloride being converted to HCl, and about 50% of the HCl being adsorbed in the direct contact evaporator. The estimated HCl emission is 10 Kg/t (20 lb/T).

Nitrogen Oxides

Nitrogen oxide emissions are calculated in Appendix D and are estimated to be 21.9 Kg/t (43.8 lb/T) for a Rapson process pulp mill.

WATER DISCHARGES

The Rapson process was developed to specifically eliminate any contaminated water discharge from a kraft mill. Minor discharges will occur from blowdown of cooking chemicals, boiler blowdown, water treatment, and runoff from wood or chip piles and cooling water. These flows contain little organic material, hence BOD will be minimal. Suspended solids of the aforementioned streams should be readily settlable and kept to a minimum.

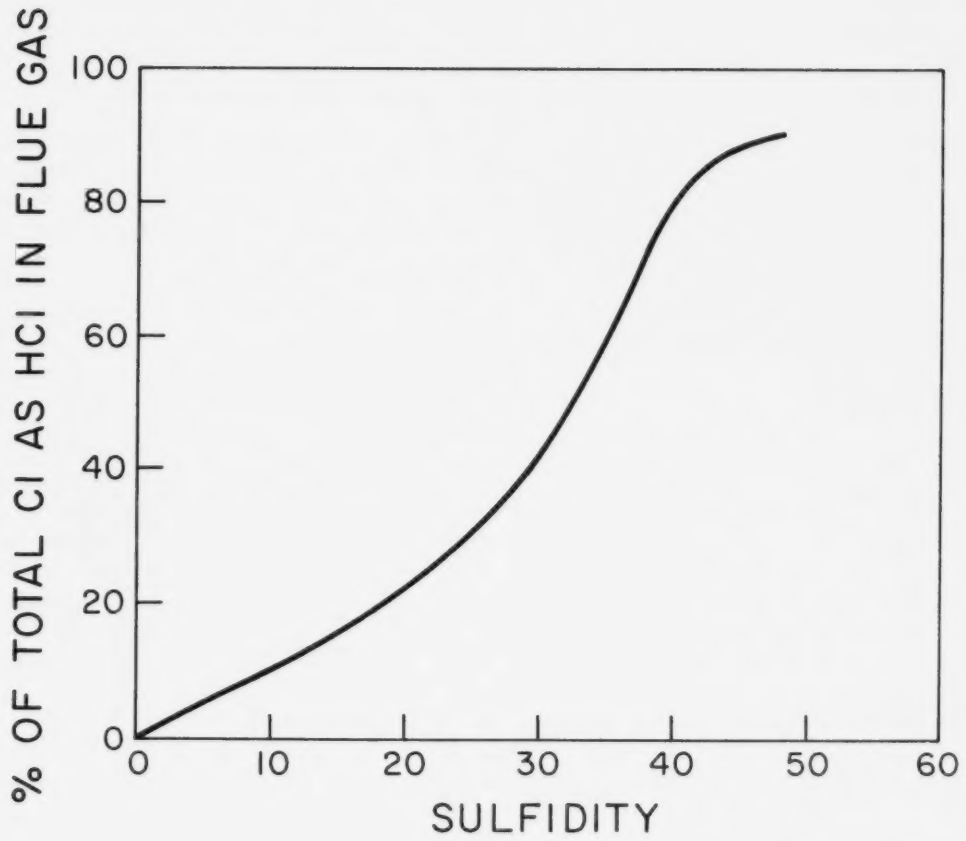

Figure 9. Percent hydrochloric acid vs. sulfidity

SOLID WASTES

Solid wastes from the Rapson process occur from 3 main sources: 1) process losses including wood preparation, green liquor dregs, drying wastes, and spills; 2) water treatment sludges; and 3) fly ash.

Process losses will largely be made up of sand, silt, and bark fines from wood preparation, and green liquor dregs. Green liquor dregs will present a dewatering problem as they are quite hydrous (44). Fly ash production will be less than that of kraft because of the lower energy requirements.

Because the Rapson process has no process effluent, and thereby no need for a biological treatment plant, there will be no biological solids generated to be disposed of. Reuse of process waters within the mill will reduce the amount of fresh water required by the mill and thereby result in a decrease in the quantity of water treatment solids produced.

Overall, the Rapson process will have a decreased solids handling problem in comparison with the kraft process.

ENERGY

The addition of the Rapson process to a kraft mill changes energy use patterns throughout the mill. Evaporation of white liquor to affect crystallization of sodium chloride requires 940 KKcal/t (3384 KBTU/T) bleached pulp. White liquor evaporation energy requirements are offset by the additional organic load to the recovery furnace from the bleach plant effluent and from the energy savings due to counter current water use in the bleach plant. Organic materials recovered from the bleach plant result in an additional 710 KKcal/t (2556 KBTU/T) being produced in the recovery furnace. Energy savings due to counter current washing in the bleach plant are 452 KKcal/t (1627 KBTU/T) bleached pulp. Overall the Rapson process requires less purchased energy than does a kraft mill, but if a new kraft mill were to use many of the energy saving processes proposed for the Rapson mill, the kraft mill would be more energy self reliant.

A Rapson process mill will need to purchase 1050 KKcal/t (3780 KBTU/T) worth of fuel, of which 852 KKcal/t (3067 KBTU/T) will be in the form of oil or gas to fire the lime kiln. The remainder of 198 KKcal/t (712 KBTU/T) will come from hog fuel or other purchased fuel. Energy calculations are presented in Appendix A.

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APPENDIX A

ENERGY USE CALCULATIONS

Many factors determine a pulp mill's energy balance. Many of the major ones can be determined. Many minor factors, such as those differences in energy usage among individual pieces of equipment or usage of secondary steam, will create variations from basic energy consumption for any type of process. The energy balances presented here are to determine basic energy use of each type of pulping process. Actual energy usage will vary somewhat depending upon the process options taken.

The pervading factor in the quantity of energy that must be provided for a pulp mill by burning purchased fuels is the quantity of energy recoverable from the dissolved wood constituents contained in the black liquor. Low energy production at the recovery furnace will require that power boiler capacity be added to take up the energy slack. The quantity of energy produced in the recovery boilers will depend both upon the heat value and the quantity of the black liquor. The black liquor heat value and quantity are determined by the yield and the quantity and type of cooking chemicals used. There are widely varying types of cooking chemicals and yield in the processes considered in this paper and, therefore, widely varying energy productions in the recovery furnaces.

Other major energy users in pulp mills are the energy required for pulping, evaporation of black liquor, pulp washing, preparation of pulping and bleaching chemicals, and heat used in the bleach plant. Oxygen pulping systems are unique in the energy requirements for pulping in that the oxidation of lignin to carbon dioxide liberates substantial quantities of energy. The oxygen digestors will probably liberate more heat than they consume. Evaporation of black liquor will require similar quantities of energy for each of the pulping processes considered in this paper.

Bleaching chemicals can be produced either in plant or outside the plant. The production of pulping and bleaching chemicals was included in the report because this energy would be consumed somewhere and the impact on the environment displaced. The amount of heat used in the bleach plant will depend upon the bleaching sequence used and the amount of countercurrent washing practiced.

The approach taken in the calculations is to determine the steam production expected from the recovery furnace and balancing that against steam

and electrical energy consumption throughout the mill. Liquor heating values are estimated and a heat balance around the recovery furnace is made. Steam usage in pulping, black liquor evaporation, pulp washing, chemical preparation, bleaching, and miscellaneous and auxiliaries are estimated.

TABLE A-1. BLACK LIQUOR COMPOSITIONS

	Kraft	Soda	Soda Semi-Chemical	Oxy. Soda	Oxy. T. Mech.	Oxy. Chip	Halogen	Rapson
Unbleached yield, %	47	47	75	50	49	53	58	40
Bleached yield, %	40	40	68	45	44	48	58	40
Cooking liquor charge, % chemical on wood	15	18	10	15	20	15	5.1	15
$(NaOH)_2$ Kg/KKg wood	177	232	32	167			66	177
Na_2S Kg/KKg wood	74							74
Na_2CO_3 Kg/KKg wood	41		127	52				41
$NaHCO_3$ Kg/KKg wood					300	225		
Na_2SO_4 Kg/KKg wood	13							13
NaCl Kg/KKg wood							76	104
NaI Kg/KKg wood						35		
Inorganics Kg/KKg pulp	305	232	159	219	300	260	142	409
Total inorganics, Kg/KKg pulp	651	494	212	438	612	490	244	1022
Inorganics recirculated Kg/KKg pulp	124	94	32	32	178	112	31	240
Washing losses, Kg/KKg pulp	15	15	7	2	14	14	0	0
Inorganics to recovery, Kg/KKg pulp	512	385	173	402	420	364	213	781
Organics dissolved, Kg/KKg wood	530	530	250	500	510	470	420	600
Kg/KKg unbleached pulp	1128	1128	333	1000	1040	887	724	1500
Organic losses, volatiles from digestor	20	20	6	18*	18*	16*	13	20
Oxidized in digestor, Kg/KKg pulp	0	0	0	50	200	200	0	0
Volatiles from evaporator, Kg/KKg pulp	8	8	2	7	7	6	5	8
Washing loss, Kg/KKg pulp	32	32	10	5	32	32	0	0
Tall soap skimmings, Kg/KKg pulp	30	30	0	30	0	0	0	30
Total organic loss, Kg/KKg unbleached pulp	90	90	12	110	257	254	18	50
Collected organics, Kg/KKg pulp	1038	1038	321	890	783	633	706	1450
Collected inorganics, Kg/KKg pulp	512	385	173	402	420	364	213	781
Total solids to evaporator, Kg/KKg unbleached pulp	1550	423	494	1292	1203	997	919	2231
% Organics in black liquor solids	67.0	72.9	65.0	68.9	65.1	63.5	76.8	65.0
% Inorganics in black liquor solids	33.0	27.1	35.0	31.1	34.9	38.1	19.2	33.8
% Lignin in black liquor solids	32.2+	35.0	32.5	33.1	26.0	25.4†	57.6	31.2
% Carbohydrates in black liquor solids	34.8	37.9	32.5	35.8	39.1	38.1	19.2	33.8
Total Solids to evaporator, Kg/KKg bleached pulp	1821	1672	544	1436	1340	1100	919	2231

*From Reference 16
+From Reference 51
†From Reference 52

TABLE A-2. CALCULATED HEAT VALUES
Basis: 1 Kg Black Liquor Solids, All Values as M cal/Kg

	Enthalpy Mcal/mole	Kraft	Soda	Soda Semi-Chemical	Oxy. Soda	Oxy. T. Mech.	Oxy. Chip	Halogen	Rapson
Input									
$(NaOH)_2$	-222	544	770	200	674	0	0	307	431
Na_2S	- 99	102	0	0	0	0	0	0	80
Na_2CO_3	-276	115	0	728	192	909	822	0	91
Na_2SO_4	-328	32	0	0	0	0	0	0	26
NaCl	-200	0	0	0	0	0	0	247	304
NaI	-200	0	0	0	0	0	66	0	0
Lignin	-142	243	264	245	250	196	192	435	236
Carbohydrates	-197	508	553	247	522	571	556	280	493
TOTAL		1544	1587	1420	1638	1676	1636	1269	1661
Combustion Products									
Na_2CO_3	-270	756	918	945	999	864	918	351	594
Na_2SO_4	-331	433							349
CO_2	- 94	2641	2801	2716	2670	2717	2651	3431	2519
H_2O	- 68	1537	1728	1393	1619	1332	1305	1660	1455
NaCl	-190	0	0	0	0	0	0	247	304
NaI	-190	0	0	0	0	0	66	0	0
Total		5367	5447	5054	5288	4913	4940	5689	5221
Theoretical heat value		3823	3860	3634	3650	3237	3304	4420	3315
Heat required for SO_4 reduction	232	303							245
Heating value		3520	3860	3634	3650	3237	3304	4420	3315

TABLE A-3. FLUE GAS COMPOSITION
Basis: 1T Black Liquor Solids, All Values in Kgram Moles

	Kraft	Soda	Soda Semi-Chemical	Oxy. Soda	Oxy. T. Mech.	Oxy. Chip	Halogen	Rapson
Moles carbon in lignin	17.2	18.7	17.3	17.3	13.9	13.5	30.4	16.6
Moles carbon in carbohydrates	13.2	14.5	12.5	13.7	15.0	14.6	7.4	11.9
Moles CO_2	30.5	33.2	29.8	31.4	28.9	28.2	37.8	28.6
Moles alkali (as Na_2O)	2.4	3.4	.9	3.0	0	0	1.3	1.8
Moles CO_2 in flue gas	28.1	29.8	28.9	28.4	28.9	28.2	36.5	26.8
Moles Na_2CO_3 formed	2.4	3.4	.9	3.0	0	0	1.3	1.8
Moles Na_2CO_3 present	.4	0	2.6	.7	3.2	3.4	0	.4
Total moles Na_2CO_3	2.8	3.4	3.5	3.7	3.2	3.4	1.3	2.2
Moles hydrogen in lignin	19.3	21.0	19.5	19.9	15.6	15.2	34.6	18.7
Moles hydrogen in carbohydrate	20.9	22.7	19.5	21.5	23.5	22.9	11.5	20.3
Total moles H_2	40.2	43.7	39.0	41.3	39.1	38.1	46.1	39.0
Moles H_2O formed from hydrogen in organics	20.1	21.9	19.5	20.7	19.5	19.1	23.0	19.5
Moles H_2O by other reactions	2.4	3.4	.9	3.0	0	0	1.3	1.8
Moles H_2O, Total	22.5	25.3	20.4	23.7	19.5	19.1	24.3	21.3
Moles oxygen in lignin	5.4	5.8	5.4	5.5	4.3	4.2	9.6	5.2
Moles oxygen in carbohydrate	9.3	10.1	8.7	9.5	10.4	10.2	5.1	9.0
Moles oxygen required for CO_2	61.0	66.4	59.6	62.8	57.8	56.4	75.6	57.2
Moles oxygen required for H_2O	20.1	21.9	19.5	20.7	19.5	19.1	23.0	19.5
Moles oxygen required for SO_4	3.1	--	--	--	--	--	--	3.1
Total O_2 required	69.5	72.3	65.0	68.4	62.6	61.1	83.9	65.6

TABLE A-4. RECOVERY FURNACE GAS MASS BALANCE

	Kraft	Soda	Soda Semi-Chemical	Oxy. Soda	Oxy. T. Mech.	Oxy. Chip	Halogen	Rapson
Black liquor concentration	50	50	50	50	50	50	50	50
% Excess air	22.5	22.5	22.5	22.5	22.5	22.5	22.5	22.5
Temp. leaving DCE, °F	300	300	300	300	300	300	300	300
Excess air at DCE inlet	21.5	21.5	21.5	21.5	21.5	21.5	21.5	21.5
Temperature of gas entering DCE	480	480	480	480	480	480	480	480
Flue gas quantities								
CO_2 Kg/Kg from black liquor solids	1.236	1.311	1.272	1.250	1.272	1.241	1.606	1.179
SO_2	.004							.004
O_2	.347	.360	.324	.341	.341	.305	.419	.327
N_2	4.484	4.644	4.193	4.412	4.039	3.942	5.412	4.232
Total dry gas	6.071	6.336	5.793	6.003	5.652	5.488	7.438	5.743
Moisture								
From air	.077	.080	0.071	0.075	0.069	0.068	0.092	0.072
From H_2 from black liquor solids	.405	.455	.367	.427	.351	.343	0.437	0.383
From black liquor water	1.000	1.000	1.000	1.000	1.000	1.000	1.000	1.000
Total Moisture	1.482	1.535	1.439	1.502	1.420	1.411	1.530	1.456

TABLE A-5. RECOVERY FURNACE HEAT BALANCE
Basis: 1T lbs, All Values as KKcal/T bls

	Kraft	Soda	Soda Semi-Chemical	Oxy. Soda	Oxy. T. Mech.	Oxy. Chip	Halogen	Rapson
Heat Input								
Calorific value of bls	3823	3860	3634	3650	3237	3304	4420	3560
Sensible heat of bls	100	100	100	100	100	100	100	
Sensible heat of miscellaneous water	26	26	26	26	26	26	26	26
Total heat input	3949	3986	3760	3776	3363	3430	4546	3686
Heat Distribution								
Sensible heat of dry flue gas	178	186	170	176	166	161	218	168
Sensible heat of moisture in flue gas	87	90	84	88	83	83	90	85
Latent heat of moisture in flue gas	881	840	790	824	780	775	830	799
Reduction of sodium sulfate	309							243
Heat of fusion of smelt	12	9	12	11	12	13	8	12
Sensible heat of smelt	86	71	91	81	91	95	61	91
Loss due to radiation	79	80	75	76	67	69	91	74
Heat in gross steam generated	2317	2710	2538	2520	2164	2234	3248	2214
Total heat distribution	3949	3986	3760	3776	3363	3430	4546	3686
Gross steam generated g/g bls	3.66	4.28	4.01	3.98	3.42	3.53	5.13	3.50
Steam used to heat liquor g/g bls	.04	.04	.04	.04	.04	.04	.04	.04
Net steam available from recovery g/g bls	3.62	4.24	3.97	3.94	3.38	3.49	5.09	3.46
Net steam available, Kg/t pulp	6592	7089	2160	5658	4529	3839	4678	7713
Net steam available, KKcal/t	4172	4487	1367	3582	2862	2430	2961	4882
Steam used for electricity generation	1341	1442	439	1151	921	781	952	1569
Steam available for process heat, KKcal/t	2832	3045	928	2430	1945	1649	2009	3313

TABLE A-6. PULPING ENERGY BALANCE

	Kraft	Soda	Soda Semi-Chemical	Oxy. Soda	Oxy. T. Mech.	Oxy. Chip	Halogen	Rapson
Stage 1, Digestion								
Basis: 1 metric ton bleached pulp								
Liquor to wood ratio	3:1	3:1	3:1	3:1	--	4:1	--	3:1
Fresh liquor to digestor, at 50°C	4.2	4.8	2.95	4.2	0.7	3.9	.6	5.0
Recirculated black liquor, at 80°C	2.1	2.1	1.4	2.1	--	3.9	--	2.5
Water in wood at 20°C	2.1	1.9	1.2	1.7	1.8	1.6	1.5	2.1
Total water to digestor	8.4	8.8	5.55	8.0	2.5	9.4	2.1	9.6
Fresh chemical to digestor	.65	.49	.21	.44	0	.49	0	1.02
Recirculated chemicals to digestor	.12	.09	.03	.03	0	.11	0	.24
Wood to digestor	2.5	2.3	1.45	2.0	2.1	2.0	1.7	2.5
Digestor temperature	180°C	180°C	170°C	170°C	160°C	130°C	160°C	180°C
Heat required to heat water	1108	1154	667	958	254	686	212	1254
Heat required to heat chemical	26	19	8	15	0	12	0	42
Heat required to heat wood	228	210	124	171	168	125	136	228
Total heat required, KKcal/t pulp	1362	1383	799	1144	422	823	348	1524
Recovered heat	672	704	389	560	0	280	0	768
Heat produced from oxidation						1000		
Stage 2, Refiner Energy, KKcal/t Pulp			34		136		136	
Stage 3, Digestion								
Consistency								
Fresh liquor to Digestor at 50°C				2.0	2.6		0	
Recirculated black liquor at 80°C				2.1	7.2		9.4	
Water from previous stage at temperature				5.9	2.5		2.1	
Total water to digestor				10.0	12.3		11.5	
Fresh chemicals to digestor				.05	.18		.03	
Recirculated chemical				--	.01		.09	
Wood to digestor				1.04	1.74		1.74	
Heat from previous stage								
Digestor temperature				120°C	160°C		80°C	
Heat required to heat water from 50°C				816	878		50	
Heat required to heat chemical				1	6		0	
Heat required to heat wood				23	0		0	
Total heat required				840	884		50	
Heat produced from oxidation				265	1000			
Recovered heat				200	750		0	
Total heat required for pulping, KKcal/t	690	679	444	963	-308	-457	531	756

TABLE A-7. PULP WASH ENERGY REQUIREMENTS

	Kraft Evaporator Condensate/ Fresh	Soda Evaporator Condensate/ Fresh	Soda Semichemical Evaporator Condensate/ Fresh	Oxygen Soda Evaporator Condensate/ Fresh	Oxygen Thermo-mechanical Evaporator Condensate/ Fresh	Oxygen Chip Evaporator Condensate/ Fresh	Chlorine Dioxide Bleach Plant	Rapson Bleach Plant
Quantity of wash water KKg/t	7.6/3.5	7.9/3.0	8.4/5.1	6.5/3.5	5.9/6.6	5.2/5.9	9.1	9.1
Temperature of cold water, °C	40/20	40/20	40/20	40/20	40/20	40/20	40	40
Temperature of wash water, °C	90	90	90	90	90	90	90	90
Temperature rise, °C	50/70	50/70	50/70	50/70	50/70	50/70	50	50
Energy required KKcal/t	380/245	395/210	420/357	325/224	295/462	260/413	455	455
Total energy* required KKcal/t	625	605	777	549	757	673	455	455

*Most of the heat used for heating wash water is low temperature heat recovered from the pulping process.

TABLE A-8. EVAPORATOR ENERGY REQUIREMENTS

	Kraft	Soda	Soda T-Chem.	Oxy. Soda	Oxy. T. Mech.	Oxy. Chip	Halogen	Rapson
Total water to evaporators, KKg/t	7.7	7.9	6.4	9.0	7.2	7.9	5.2	8.5
Solids in black liquor to evaporators, KKg/t	1.82	1.67	0.54	1.44	1.34	1.10	0.92	2.23
Water in strong black liquor, KKg/t	1.8	1.7	0.5	1.4	1.3	1.1	0.9	2.2
Water evaporated, KKg/t	5.9	6.2	5.9	7.6	5.9	6.8	4.3	6.3
Steam required (4.7 Kg evap./ Kg steam)	1.3	1.3	1.3	1.6	1.3	1.45	.9	1.3
Energy required, KKcal/t	770	770	770	948	770	859	533	770

Bleach Plant Energy Calculations

Three bleach plant models were chosen by which to calculate steam requirements of the bleach plant: 1) a full CEDED sequence with no water reuse, 2) a full C/D-EDED sequence with direct counter current water reuse (53), and 3) a DED sequence with water reuse. The first sequence is to represent the energy use in a bleach plant at a standard kraft, soda, or soda thermochemical mill. The second sequence applies to the Rapson process, and a standard kraft mill utilizing bleach plant water reuse. The third sequence applies to oxygen and halogen pulping processes. In each case the energy required was caluclated from the energy to heat the wash water from 35^{o} to the temperature required in the subsequent bleach or extraction stage. Tables A-9 through A-11 show the calculations.

TABLE A-9. HEAT REQUIREMENTS OF A CEDED BLEACHING SEQUENCE

Schedule	C	W	E	W	D	W	E	W	D	W
Consistency, %	3		10		10		10		10	
Temperature, ^{o}C	15		50		60		50		70	
Wash water flow/KKg/t		11.5		11.5		11.5		11.5		11.5
Wash water temperature req. ^{o}C		55		65		50		75		50
ΔT		40		50		35		60		35
Heat required, KKcal/t		460		570		402		690		402
Total heat required, KKcal/t = 2524										

TABLE A-10. HEAT REQUIREMENT OF A C/DEDED BLEACHING SEQUENCE WITH FULL COUNTER CURRENT WATER REUSE

Schedule	C/D	W	E	W	D	W	E	W	D	W
Consistency, %	3		10		10		10		10	
Temperature, ^{o}C	25		50		60		50		70	
Wash water flow, KKg/t		13.5		11.3		10.5		10.5		11.3
Temperature of water from Previous stage, ^{o}C		50		50		50		45		15
Wash water temperature required, ^{o}C		55		65		60		75		50
ΔT, ^{o}C		5		15		0		30		35
Heat required, KKcal/t		68		120		0		315		395

Total heat required = 948 KKcal/t

TABLE A-11. HEAT REQUIREMENTS OF A DED BLEACHING SEQUENCE WITH FULL COUNTER CURRENT WATER REUSE

Schedule	D	W	E	W	D	W
Consistency, %	10		10		10	
Temperature, ^{o}C	60		50		70	
Wash water flow, KKg/t		10.5		10.5		11.3
Temperature of water from previous stage, ^{o}C		50		45		15
Wash water temperature required, ^{o}C		50		75		50
ΔT, ^{o}C		0		30		35
Heat required, KKcal/t		0		315		395
Total heat required = 710 KKcal/t						

TABLE A-12. MILL ENERGY BALANCE
All Values are KKcal/t Bleached Pulp

	Kraft	Soda	Soda T-Chem	Oxy. Soda	Oxy. T-Chem	Oxy. Chip	Halogen	Rapson
Wood Preparation	111	111	70	104	106	120	90	111
Pulping								
Steam	690	679	444	963	-444	-457	395	756
Electrical	109	109	100	190	136	53	136	109
Total	799	788	544	1153	-308	-404	531	865
Chemical Recovery								
Pulp washing	625	605	777	594	757	673	455	455
Evaporation	770	770	770	948	770	859	533	770
Recovery furnace	-4172	-4487	-1367	-3582	-2862	-2430	-2961	-4882
Causticizing	852	1117	91	714	0	0	219	852
White liquor evaporation	0	0	0	0	0	0	0	943
Oxygen manufacture	0	0	0	181	728	729	0	0
Chlorine manufacture	204	204	0	--	--	--	--	204
ClO_2 manufacture	306	306	306	306	306	306	1480	300
Electrical	165	165	200	230	300	170	200	270
Total	-1223	-1320	777	-609	-1	306	-74	1088
Bleaching								
Steam	1400	1400	710	710	710	710	710	948
Electrical	90	90	90	54	54	54	54	90
Total	1490	1490	800	764	764	764	764	1038
Miscellaneous and auxiliary	220	220	220	220	220	220	220	220
Pollution Control								
Water treatment	80	80	80	55	55	55	0	0
Air treatment	10	10	10	10	10	10	15	15
Total	90	90	90	65	65	65	15	15
Total Purchased Energy	1349	1268	2501	1548	740	951	1456	1050
Causticizing	852	1117	91	714	0	0	219	852
Power boiler capacity	492	151	2401	834	740	951	1237	198

Chlorine and Chlorine Dioxide Production Energy Requirements

Between 2,400 KWH to 3000 KWH is required to produce a ton of chlorine in diaphragm cells. Normally about 10,000-12,000 lb of steam is required to concentrate each ton of caustic from 10-12% to approximately 50% NaOH. Concentration of caustic won't be necessary for on-site production of chlorine because shipping is not required.

Chlorine dioxide requires 5,425 KWH per metric ton of $NaClO_3$ produced in a Krebs cell. Chlorine dioxide is produced from $NaClO_3$ in a R3 generator, using HCl as the reducing agent. HCl is available from chlorine production; 1.08 tons per ton of chlorine dioxide will be required. Chlorine dioxide generators produce a mixture of chlorine dioxide and chlorine in about a 65:35 weight ratio. In chlorine dioxide pulping, this chlorine dioxide is used as the total mixture with the chemical requirement expressed as total chlorine.

For one metric ton of $ClO_2 + Cl_2$ as chlorine, 1.50 tons of $NaClO_3$ and 1.03 tons of HCl, or 1.0 tons of chlorine and hydrogen are required. Production of 1.50 tons of sodium chlorate will require 8137.5 KWH and production of 1.0 tons of chlorine will require 3304 KWH. Burning of the chlorine and hydrogen will provide considerable energy that can be used for the generation of some of the electrical power needed. Each ton of $ClO_2 + Cl_2$ as chlorine will require 11,442 KWH or 9847 KKcal. Halogen pulping will require 0.15 tons Cl per ton pulp produced, or 1480 KKcal of energy per ton pulp.

APPENDIX B

POWER BOILER SO_2 EMISSIONS

1. Assume use of oil containing 1.8% sulfur in the power boiler. Oil has a heating value of 149,000 BTU/gal. Assume oil weighs 8 lbs per gallon. The quantity of sulfur dioxide produced in a power boiler fired with oil is 3.4 g/KKcal.

2. Assume use of coal containing 1.9% sulfur and with a heating value of 13,000 BTU/lb. The quantity of sulfur dioxide produced in a power boiler fired with coal is 5.3 g/KKcal.

3. Waste wood has a sulfur content such that it will produce 0.67 Kg/KKcal of energy produced.

TABLE B-1. CALCULATION OF SO_2 EMISSIONS

	Kraft	Soda	Soda Semi-Chem	Soda	Therm	Chip	ClO_2	Rapson
Energy required KKcal/KKg pulp	492	151	2401	834	740	951	1237	198
SO_2 emissions for:								
Oil fired Kg/KKg pulp	1.7	0.5	8.2	2.8	2.5	3.2	4.2	0.7
Coal fired Kg/KKg pulp	2.6	0.8	12.7	4.4	3.9	5.0	6.6	1.0
Waste wood Kg/KKg pulp	0.3	0.1	1.6	0.6	0.5	0.6	0.8	0.1

APPENDIX C

PARTICULATE EMISSIONS

Particulate emissions from a recovery furnace are affected by a number of recovery furnace operations such as firing rate, heating value of the black liquor, water content of the black liquor, furnace temperature, primary and secondary air temperature, black liquor chemical makeup, excess air, particulate control equipment efficiency, chemical and physical nature of the particulates, and process configuration (54). Prediction of particulate emissions from a soda mill recovery furnace is difficult, although some trends are evident.

Particulate emissions from a recovery furnace originate in the volatilization of sodium and sodium compounds from the smelt on the furnace bed, and from carryover of fine ash particles resulting from spraying of the black liquor (49), (55). The larger particules resulting from carryover of ash are easily removed. Volatilized sodium and sodium compounds condense and react with available carbon dioxide and sulfur dioxide to form a fume. The amount of fume formed depends upon the amount of sodium vaporized, which is in turn governed by the bed temperature and the sulfidity of the black liquor. The higher the bed temperature, the more volatilization of particulates. Low sulfidities, or the lack of sulfur altogether, causes higher particulate emissions.

Assuming all conditions other than the heating value of the black liquor are held constant in the recovery furnace for each pulping process, a comparison of the expected particulate emissions can be made from those processes.

If halogens, either the chloride or iodide, are present in the black liquor, greater particulate emissions can be expected. Halogens vaporize at a much lower temperature (1413^{o}C for chlorides and 1304^{o}C for sodium iodide) than do other recovery furnace sodium compounds, hence the quantity of fumes is much larger. The quantity of halogens vaporized in the recovery furnace depends upon the proportion of halogens present and the bed temperature (42).

Table C-1 lists the various sources of particulates from a pulp mill as well as some of the operating parameters affecting particulate emissions. Calculations for the smelt tank emissions are made by comparing the quantity of smelt processed in each pulping process to the quantity used in kraft pulping and adjusting the average particulate emissions for kraft mills reported in Reference 54 accordingly. The same procedure was used for calculating lime kiln emissions, using the quantity of NaOH required for com-

TABLE C-1. Calculation of Particulate Emissions

Source	Kraft	Soda	Soda Semi-Chemical	Oxy. Soda	Oxy. Therm	Oxy. Chip	ClO_2	Rapson
Recovery furnace								
Heating value of black liquor solids, cal/g	3616	3683	3171	3730	2781	3097	4492	3125
Halogen content of white liquor, %				13		13	73	30
Fumes formed, g/l	.0209	.038	.015	.040	.008	.014		
Gas flow, KKl/t	7.43	6.20	1.95	5.82	5.48	4.18		
Emissions prior to ESP, Kg/t	155	236	29	233	44	57		
Emissions to atmosphere, Kg/t	1.55	236	0.29	2.33	0.44	0.59	1.2	4.0
Smelt tank								
Smelt processed, Kg/t	513	494	206	424	595	490	202	880
Particulate emissions, Kg/t	.25	.24	.1	.21	.29	.23	.10	.43
Lime kiln								
NaOH required, Kg/t	144	232	32	47	0	0	--	144
Lime required, Kg/t	92	145	21	30				92
Particulate emissions	.50	.81	.11	.16	0	0	0	.50
Power boiler								
Energy required, KKcal/t pulp	492	151	2401	834	740	951	1237	198
Particulate emissions:								
Fuel								
Gas @ 5 g/10^6 KJ	--	--	--	--	--	--	--	--
Oil								
Coal	.4	.12	1.97	.69	.61	.78	1.02	.16
Wood waste	.52	.16	2.52	.88	.78	1.0	1.30	.21
Total particulates, Kg/t	2.8	2.7	3.0	3.6	1.5	1.8	2.6	5.1

parison. Power boiler emissions are calculated from the energy requirements of each type of mill for the fuels, gas, oil, coal, and wood waste.

APPENDIX D

NO_x EMISSIONS CALCULATIONS

The quantities of nitrogen oxides emitted from a power boiler is dependent upon the flame temperature, and hence the fuel used. NO_x emissions for various fuels as a function of power produced for power boilers are: bituminous coal, 0.00163 g/Kcal; residual fuel oil, 0.00096 g/Kcal; natural gas, 0.00067 g/Kcal; and waste wood 0.0018 g/Kcal (2), (56).

TABLE D-1. POWER BOILER NO_x EMISSIONS

	Kraft	Soda	Soda Semi Chem.	Oxy. Soda	Oxy. Therm.	Oxy. Chip	ClO_2	Rapson
Energy required KKcal/t pulp	492	151	2401	834	740	951	1237	198
No_x emissions Kg/t pulp for:								
Oil fired	.47	.14	2.30	.80	.71	.91	1.19	0.19
Coal fired	.80	.25	3.91	1.36	1.21	1.55	2.02	0.32
Natural gas	.33	.10	1.61	0.56	0.50	0.64	0.83	0.13
Waste wood	.89	.27	4.32	1.50	1.33	1.71	2.23	0.36

Nitric oxides are also formed in the recovery furnace and in the lime kiln. Nitric oxide concentrations in the recovery boiler are relatively low because of the low flame temperature. High flame temperatures result in higher NO_x formation. Lime kilns have higher flame temperatures and consequently result in higher nitric oxide emissions. Table D-2 shows calculations for NO_x emissions from the recovery furnace and lime kiln. The estimates were made by using a NO_x emission of 3 kg/t (6 lb/T) from a kraft furnace, and 18 kg/t (36 lb/T) NO_x from a kraft lime kiln, and scaling the other types of mills according to the energy production in the recovery furnace, or the energy consumption in the lime kiln, respectively.

TABLE D-2. RECOVERY FURNACE AND LIME KILN NO_x EMISSIONS

	Kraft	Soda	Soda Semi Chem.	Oxy. Soda	Oxy. Therm.	Oxy. Chip	ClO_2	Rapson
Recovery furnace energy production, KKcal/t	4172	4487	1367	3582	2862	2430	2961	4882
Recovery furnace NO_x emissions, Kg/t	3.0	3.2	1.0	2.6	2.1	1.7	2.1	3.5
Lime kiln energy use, KKcal/t	852	1117	91	714	0	0	219	852
Lime kiln NO_x emissions, Kg/t	18.0	23.6	1.9	15.1	0	0	4.6	18.0

APPENDIX E

SULFUR LOADINGS TO NON-SULFUR PULPING PROCESSES

Although no sulfur compounds are intentionally added to non-sulfur pulping processes, sulfur compounds are inadvertantly introduced into the cooking liquors and recovery process. Sulfur compounds accumulate in the cooking liquors until they are purged from the system. Sulfidities of about 5% can result from sulfur accumulations. Reduced sulfur emissions from pulp mills result even at the low sulfur levels found in non-sulfur pulping.

Sulfur is introduced into the pulping chemical cycle from several sources. Sulfur dioxide, produced by burning sulfur containing fuel oil in the lime kiln, reacts with the lime to produce calcium sulfate. During the causticizing step, the sulfate is transferred to the pulping liquor. About 0.5 pounds of sulfur per ton pulp is added to the cooking liquor from fuel oil via causticizing. About 0.021 lbs sulfur per ton pulp enters the mill via purchased limestone (57). Sulfur enters a mill through the mill raw water supply. The amount of sulfur added by the water supply will vary by location, depending upon water quality. Some waters are naturally high in sulfates. Treatment of surface waters with alum will contribute additional sulfur to the mill.

The level to which sulfur accumulates in the cooking liquor depends upon a balance between the sulfur input and sulfur losses. As the concentration of sulfur in the cooking cycle increases, the quantity of sulfur lost increases. Sulfur losses are through the chemical recovery flue gas, malodorous emissions, losses through the brown stock washer system, losses in the green liquor clarification dregs, and losses in the causticizing department.

Sulfur accumulation in a non-sulfur pulping mill cooking cycle may result in odor emissions from various sources. Table E-1 lists sources and quantities of reduced sulfur emissions from a soda mill prior to odor control measures (57).

Odors from a non-sulfur mill can be effectively controlled by chemically scrubbing the gases containing the malodorous compounds with oxidants. Collection and scrubbing of the low pressure feeder and S.V. relief condenser gases would eliminate 98% of the odor. These gases can be scrubbed with hydrochlorite filtrate, chlorine filtrate, spent acid, and bleach plant effluent (57).

TABLE E-1. ORGANOSULFUR EMISSIONS

Source	Compound	lbs S/ADTP	%
Low pressure feeder	DMS*	0.01618	86.90
	DMDS	0.00124	
S.V. relief condenser	DMS	0.00200	11.21
	DMDS	0.00026	
#2 Diffusion washer	DMS	0.00006	0.43
	DMDS	0.00002	
15% Black liquor tank	H_2S	0.00008	1.40
	DMS	0.00002	
	DMDS	0.00016	

*DMS and DMDS stand for dimethyl sulfide and dimethyl disulfide, respectively.